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16 ABSTRACT

Four techniques for determination of water soluble sulfate in atmospheric samples were compared including the barium sulfate turbidimetric method, the Brosset (barium-Thorin) method, the automated barium-methylthymol blue procedure and a microchemical (barium-dinitro-sulfonazo III) colorimetric method developed at the Air and Industrial Hygiene Laboratory. These, in turn, were compared to x-ray fluorescence for determination of total sulfur, obtained independently at the Environmental Protection Agency's Research Triangle Park laboratory. The parameters studied included precision and accuracy employing standard solution and ambient air samples, and the influence of twelve potential interferents. The ambient air samples studied were collected at different locations throughout the U.S. so that the influence of different particle matrices could be evaluated. As supplementary objectives, analyses of particulate matter samples collected simultaneously on high volume and low volume glass-fiber filters and low volume Teflon filters, with and without size segregation, were compared. Results of the study are presented.

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COMPARISON OF WET CHEMICAL AND INSTRUMENTAL METHODS FOR MEASURING AIRBORNE SULFATE

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CONTENTS

	Page
List of Figures	v
List of Tables	vi
Acknowledgements	viii

SECTIONS

I.	Introduction	1
II.	Summary	4
III.	Set Up and Preliminary Evaluation of Methods	7
	A. Methylthymol Blue Procedure	
	B. Modified Brossat Procedure	
IV.	The Effect of Interferents on Sulfate Determinations	16
	A. Description of the Experiment	
	B. Results of Interference Studies	
	C. Time Dependence of Interference Effects with Sulfide and Sulfite	
	D. Recommendations to Eliminate Interferences	
	E. Summary and Conclusions	

V. Precision, Equivalence and Accuracy of Four Sulfate Procedures with Atmospheric High Volume Filter Samples 29

A. Description of the Experiment

B. Analytical Precision

C. Equivalence of Methods

D. Interference Effects

E. The Accuracy of the Sulfate Methods by Standard Additions

F. Summary and Conclusions

VI. Equivalency of Wet Chemical and X-ray Fluorescence Methods and Influence of Sampling Design with Atmospheric Low Volume Filter Samples 38

A. Description of the Experiment

B. Results

C. Summary and Conclusions

VII. References 47

Appendix

A. The Turbidimetric Method. 101

B. The Technicon Industrial Method No. 118-71W. 108

C. The AIHL Microchemical Method. 109

D. The Modified Brosset Method. 130

FIGURES

1 Preliminary Comparison of Turbidimetric and Methylthymol Blue Methods for Sulfate on Atmospheric Samples Collected on 24-Hour Glass Fiber High Volume Filters

2-8 Interferograms

9-22 Recovery of Sulfate from Standard Additions to Atmospheric Samples

LIST OF TABLES

1 Precision of Standard Curves for Methylthymol Blue (MABH) Analysis of Sulfate with the Technicon Auto Analyzer II

2 Comparison of the Brosset and Micro AIHL Methods for Sulfate

3 Comparison of H_2SO_4 and Na_2SO_4 Standards in Analysis by the Modified Brosset Procedure (in acetone) with 2.5 and 5.0 cm Cells Without Ion Exchange

4 Precision of H_2SO_4 and Na_2SO_4 Standards in Analysis by the Brosset Procedure in Dioxane Without Ion Exchange

5 Precision of the Modified Brosset Procedure with Ion Exchange Treatment (three filter discs)

6 Recovery of Sulfate by Modified Brosset Procedure After Treatment with Three Ion Exchange Filter Discs

7 Interference Effects in the Turbidimetric Method (ug/ml Observed Sulfate)

8 Interference Effects in the Technicon Methylthymol Blue Method (ug/ml Observed Sulfate)

9 Interference Effects in the AIHL Microchemical Method (ug/ml Observed Sulfate)

10 Interference Effects in the Modified Brosset Method, in Acetone (ug/ml Observed Sulfate)

11 Interference Effects in the Modified Brosset Method, in Dioxane (ug/ml Observed Sulfate)

12 The Effect of Aging of Interferent-Sulfate Solutions on Interference Effects by the Modified Brosset Method (in dioxane)

13 The Effect of Aging of Sulfide-Sulfate Solutions on Interference Effects by Four Methods (20 ug/ml added sulfate)

14 The Effect of Aging of Sulfite-Sulfate Solutions on Interference Effects by Four Methods (20 ug/ml added sulfate)

15A Sulfate Analysis of Atmospheric Hi-Vol Samples by Four Methods, St. Louis, MO (ug/m^3)

15B Sulfate Analysis of Atmospheric Hi-Vol Samples by Four Methods, Durham, NC (ug/m^3)

15C Sulfate Analysis of Atmospheric Hi-Vol Samples by Four Methods, Pasadena, CA ($\mu g/m^3$)

16 The Influence of Ion Exchange Treatment on High Volume Filter Samples Analysed by the AIHL Microchemical Method

17 Protocol for Standard Addition Study-High Volume Glass Fiber Filter Sample Extracts

18 Recovery of Addition of Sulfate to High Volume Glass Fiber Filter Sample Extracts (%)

19 Mean Fractional Recoveries of Sulfate with Standard Additions

20 Summary of Low Volume Fluoropore Filter Sulfate Determinations ($\mu g/m^3$ sulfate)

21 Summary of Low Volume Glass Fiber Filter Sulfate Determinations

22 Relative Results-Fluoropore Filters

23 Relative Results-Glass Fiber Filters

24 Comparison of EPA and LBL X-ray Fluorescence Results on Low Volume Fluoropore Filters

25 The Mean Fraction of Sulfate in Refined (0-2 μm) Particles

26 Summary of Comparison of Glass Fiber and Fluoropore Filter Sulfate Results as a Function of Particle Size and Sampling Site

27 Comparison of Selected Metals Concentrations by XRFA in Total and Refined Particle Samples ($\mu g/m^3$)

28 Comparison of Low (0-20 μm) and High Volume Glass Fiber Filter Sulfate Results

29 Comparison of Fluoropore (0-20 μm) and Glass Fiber High Volume Filter Sulfate Results

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I. INTRODUCTION

As a consequence of the present energy crisis and the limited supply of natural gas and low sulfur oil, use of fuels of higher sulfur content is increasing. The adverse implications for human health of particulate sulfate together with the likelihood of higher atmospheric loadings for this material make essential the use of rapid, sensitive, accurate, specific, and precise analytical methods to determine the levels of atmospheric sulfate. Validated methods are especially required for determining sulfate in the range of 1 to 10 μg/ml such as are often obtained with extracts from 1 to 2 hour size-segregated aerosol samples. As part of existing programs, the Air and Industrial Hygiene Laboratory (AIHL) has previously begun evaluation of both instrumental and wet chemical methods for aerosol analysis including sulfate and nitrate methods. The present study complemented this work, with principal focus on comparison of methods for particulate sulfate analysis.

The objectives of the program have been to evaluate and compare procedures for sulfate determination in atmospheric particulate matter and to relate sulfate values so obtained to total sulfur determinations by x-ray fluorescence analysis (XRFA) using samples collected in several geographic areas differing in pollutant composition. The specific goals of the evaluation effort include:

1. Evaluation of the precision and accuracy of each of the sulfate methods employing synthetic and atmospheric samples from several locations.

2. Evaluation of the influence of likely interferents on the apparent sulfate values.

Since the degree of interference in analytical methods may be dependent on particle size, as with XRFA, or on the concentration of interfering species which are principally associated with small or large particles sizes in atmospheric aerosols, size-segregated samples are included in this study. The present study has examined five analytical methods for water soluble sulfate or total sulfur:

1. The $BaCl_2$ turbidimetric procedure (Appendix A).
2. The methylthymol blue procedure as automated for the Technicon Auto Analyser II (MTB) (Appendix B).
3. The AIHL microchemical procedure (Appendix C)
4. A modified Brosset procedure (Appendix D)
5. X-ray induced x-ray fluorescence (XRFA)

Ambient air samples were collected at three locations, Durham, NC; St. Louis, MO; and Pasadena, CA; to obtain varied particle matrices. Sampling in North Carolina and Missouri was conducted by the EPA staff while that in Pasadena was conducted by the AIHL staff. Sampling at each site was conducted for four days for a total of 12 days of sample collection for the study. All sample collections were on a 24-hour basis. Sampling equipment consisted of a hi-volume sampler and two "T samplers". Each "T sampler" contained both a total and a refined particle sampler. Filter media and sampling conditions were as follows:

1. Hi-volume sampler -- 8 x 10" Gelman Type A glass fiber filters.
2. Total filter -- 37 mm Gelman Type A glass fiber filters, sampling at 12 l/min and collecting 0 to 20 μm particles.
3. Refined fraction filter -- 37 mm Gelman A glass fiber filters, sampling at 12 l/min and collecting 0 to 2 μm particles.
4. Total filter -- 37 mm Fluoropore (1.0 μm pore size) filters, sampling at 12 l/min and collecting 0 to 20 μm particles
5. Refined fraction filter -- 37 mm Fluoropore (1.0 μm pore size) filters, sampling at 12 l/min and collecting 0 to 2 μm particles.

Wet chemical analysis of these as well as synthetic samples was carried out at AIHL while XRFA was carried out both at the Environmental Protection Agency's Research Triangle Park Laboratory (EPA-RTP), and at the Lawrence Berkeley Laboratory (LBL) under subcontract to AIHL.

II. SUMMARY

A program has been conducted to evaluate and compare four wet chemical methods and x-ray fluorescence analysis for determination of sulfate in atmospheric samples. The four chemical methods studied were the $BaCl_2$ turbidimetric, automated methylthymol blue (MTB), AISI microchemical and a modified Brosset procedure. The specific parameters evaluated included the equivalency of the methods, analytical precision and accuracy and the influence of potential interferents. The atmospheric samples used were collected in Durham, NC; St. Louis, MO and Pasadena, CA. In addition, the sampling design permitted a limited evaluation of sampling errors related to atmospheric sulfate determination. Specifically the influence of filter medium, sampling volume and particle size were evaluated.

With 24-hour high volume filter samples analytical precision with the wet chemical methods expressed as coefficients of variation, ranged from 1-5%. The methods yielded nearly equivalent results with the range of results with the three sets of samples being about 10%. While agreeing within the stated range, the MTB and modified Brosset methods gave generally higher results than the other methods. This proved to be consistent with studies of accuracy by standard additions suggesting a systematic positive bias rather than negative interference effects with the remaining methods as the cause for the lower results. The standard addition studies with the MTB method revealed positive errors of 10-20% with 63% of the experiments, 5-10% positive errors in 25% of the experiments and -5 to 5% errors in the remaining.

The degree of agreement found suggests that the choice of a method from among these four, for analysis of high volume samples can be based upon such factors as cost per determination or experimental convenience. The restricted range of both the modified Brosset and AIHL micromethod clearly makes them inappropriate for consideration with high volume samples.

The four wet chemical methods displayed widely varying sensitivities to the 12 interferents studied. The modified Brosset procedure emerged as the method least affected by the potential interferents; only sulfide and sulfite caused significant interference with this method. The degree of agreement between the four methods with high volume filter samples suggests these interferents to be of minor importance with large air samples. In what appears to be the worst case, the AIHL microchemical method results for St. Louis and Durham were shown to be about 10% low due to interference, probably by cationic interferents.

In contrast to the high volume sample results, low volume filters have revealed differences between the three wet chemical methods able to analyse these samples of up to a factor of 3 for individual samples and 1.6 when pooled by sampling site. The greater dilution of interferents from the filter medium with the high volume samples may account for the closer agreement found between methods with these samples.

XRFA results for sulfur by the Lawrence Berkeley Laboratory and Research Triangle Park differ by a factor of 1.7 for the same samples. The lack

of good agreement for sulfur in this study indicates a need for better standards and for more accurate correction for the attenuation of the soft sulfur x-rays in the filter medium. The RTP XRF measurements of total sulfur as sulfate are generally higher by 10 to 50% than the measurements by the MTB method; the LBL XRF measurements are lower than the MTB measurements by 20 to 50%.

The present data are consistent with significant artifact sulfate formation from SO_2 on the low volume glass fiber filter samples with enhanced sulfate formation in the presence of a large particle-related oxidation catalyst(s). The equivalence of low volume Fluoropore total filter and high volume glass fiber sulfate results as measured by the MTB method implies that an insignificant percentage of the sulfate determined is due to artifact sulfate formation with 24-hour high volume glass filters.

Finally, in comparing the three wet chemical methods with low volume samples, the modified Brosset procedure has, at times, yielded what is considered to be erratic behavior. In spite of the positive error in the method revealed by studies with high volume samples, the MTB method is considered the most reliable of the three for long term (e.g. 24-hour) low volume samples. For short term, low volume samples requiring a micro sulfate method we favor the AIHL microchemical method.

III. INITIAL SET UP AND EVALUATION OF METHODS

Both the AIHL micromethod and the $BaCl_2$ turbidimetric procedure have been in use for some time at AIHL and, therefore, required no further preparatory work before beginning the present program. However, the automated MTB and Brosset methods were new to the laboratory and, therefore, required both set up and preliminary evaluation to insure reliable data are obtained before beginning the methods comparison study. The present section describes these efforts.

A. The Automated Methylthymol Blue (MTB) Procedure

1. Introduction

The objective in setting up this method was to duplicate as closely as possible the technique in use at Research Triangle Park for analysis of samples from the National Air Sampling Network (NASN). Starting point for this effort was the Technicon Industrial Method No 118-71W, a copy of which is included as Appendix B. The Rockwell International Science Center, which currently uses the MTB procedure with a Technicon Auto Analyzer II, provided initial assistance. An inherent limitation in duplicating the RTP system arises from the use at RTP of the Technicon Auto Analyzer I rather than the model currently available. It is believed that the more uniform air bubbles (used to separate samples in the tubing) in the Auto

Analyser II will produce somewhat improved precision.[A]

The similarity of operating procedures used at the AIHL and EPA-RTP was confirmed by site visits.

2. Operation and Calibration of the Auto Analyser II for Sulfate Analysis

During initial operation, bubbles in the ion exchange column proved to be a source of significant unreliability. When starting the Auto Analyser there is an initial surge of air. This air surge is greater than the capacity of the debubbler preceding the ion exchange column thereby introducing air into that column. To overcome this strong surge, a by-pass and valve were introduced between the debubbler and the mixing coils. In starting up the instrument the valve is opened and the air surge goes through the by-pass. When the surge dissipates the valve is closed and the flow goes through the column without introducing air. This modification does not affect the operation but significantly decreases the down time of the instrument.

The original range for sulfate as supplied (0-300 µg/ml) was adjusted

[A]RTP has recently changed to use of the Auto Analyser II and has, indeed, found improved precision (C.V. 5% vs 7%). Accordingly, the AIHL and RTP methods are, at present, the same.

to give a recorder span of 0-60 ug/ml by using an 0.42 cm^3/min sample suction tube and a 1.6 cm^3/min stream of dilution water. The calibration cur approximately linear over the 0-60 ug/ml range.

As an initial step for running comparisons, the Auto Analyser was calibrated with sodium sulfate standards up to 100 ug/ml $SO_4^{=}$ in different positions on the sampling tray to determine memory effects. High-volume filter sample extracts which had been previously analysed for sulfate by turbidimetry were available for an initial comparison. Blanks were run separately by replacing the methylthymol blue solution with 80% alcohol and extending the sensitivity range.

1. Operating Parameters Influencing Reliability of the MTB Method Data

After one and a half hours warm up time of the Auto Analyser, blanks and standards were run on a 30 samples per hour mode. Since the turntable has 40 positions (defined as a cycle), each cycle in the mode lasts about one hour and 20 minutes. In order to compare the cycles within one day and over more extended periods of time, the regression lines from the standards were calculated and the following parameters were obtained: intercept (a), slope (b), standard deviation of intercept (S_a), slope (S_b) and the standard error of the estimate ($S_{y \cdot x}$). (Table 1.)

Table 1

PRECISION OF STANDARD CURVES FOR METHYLTHYMOL BLUE (NASH) ANALYSIS OF SULFATE WITH THE TECHNICON AUTO ANALYZER II[a]

Parameters	Cycle[b] No.	$s_{y,x}$	b	s_b	a[c]	s_a
a) Linear range 0-200 µg $SO_4^=$/ml b) No ion exchange c) 10 standard solutions at 5 concentrations + 30 water blanks	1	0.49	0.28	.002	-1.4	.25
	4	0.44	0.29	.002	-2.5	.25
a) Linear range 0-60 µg $SO_4^=$/ml b) No ion exchange c) 10 standard solutions at 5 concentrations + 30 water blanks	1	0.91	1.10	.002	-4.3	.85
	3	0.46	1.08	.011	-3.8	.43
a) Linear range 0-60 µg $SO_4^=$/ml b) 2 mm I.D. ion exchange c) 10 standard solutions at 5 concentrations + 30 water blanks	1	0.83	1.07	.012	-2.8	.45
	2	0.62	1.05	.009	-3.0	.34
a) Linear range 0-60 µg $SO_4^=$/ml b) 2 mm I.D. ion exchange c) 30 samples and 10 standard solutions	1	1.15	1.10	.023	-1.1	1.1
	2	1.33	1.15	.030	-3.0	1.3
a) Linear range 0-60 µg $SO_4^=$/ml b) 2.5 mm I.D. ion exchange c) 30 samples and 10 standard solutions	1	0.88	1.17	.020	-3.6	.83
	2	0.81	1.14	.018	-2.1	.77

a. The symbols are as follows:
   $s_{y,x}$ = standard error of the estimate
   a = intercept
   b = slope
   s_a and s_b = standard error of intercept and slope, respectively.
b. Each cycle represents running of some combination of standards, samples and water totaling 40 determinations.
c. In strip chart units, 100 units per full scale.

The results show small variations in slope and significant shifts in the intercept over the linear portion of the working curves. These findings indicated the need to either perform base line subtractions or to intermingle standards and samples using the working curve developed for a given cycle to calculate the unknown samples.

There are two relevant blanks of concern to the study of the automated MTB method, (1) the inherent color of the aqueous extract of a particulate sample, and (2) the sulfate blank from extraction of a clean filter. The sample blanks (1) were determined for a group of samples collected in Riverside, CA. For these samples the sample blank measured by substituting 80% ethanol[6] for the reagent represented < 1.0% of the measured sulfate and is considered within the uncertainty of the method. Therefore, such corrections were not determined during the remainder of this study. Filter blanks were measured for Gelman A glass fiber and proved to be 2-3 ug/ml apparent $SO_4^{=}$[66]. Cellulose filters (Whatman 41) had a zero blank.

[6]This omits HCl and $BaCl_2$ as well as the dye. The effect of omission of HCl is negligible on the final pH since a large excess of NaOH is added, relative to the acid normally present. The influence of omitting $BaCl_2$ is considered negligible as well.

[66]Extracting a 3/4" strip into 100 ml H_2O.

4. Intermethod Comparison with the MTB and Turbidimetric Methods - Preliminary Findings

Employing aqueous extracts from particulate samples collected on glass fiber filters, sulfate determinations were conducted both by the MTB and turbidimetric method. A comparison of results by the two techniques is shown in Figure 1 indicating at most a 15% difference with the MTB results consistently higher. The difference is especially marked at high concentration. Having established by preliminary studies the precision and comparability of the MTB to the turbidimetric method, it was judged adequate for beginning interference studies.

B. The Modified Brosset Procedure

1. Introduction

The starting point for this method is the work by Brosset and Ferm.[1,2] As detailed therein, the method is semi-automated and employs custom-made glassware. Since it was not considered feasible to duplicate this system in the time available, methods referred to here as "modified Brosset procedures" were established and evaluated.

The Brosset procedure is based on the change in color brought about by the reaction:

PRELIMINARY COMPARISON OF TURBIDIMETRIC AND METHYLTHYMOL BLUE METHODS FOR SULFATE ON ATMOSPHERIC SAMPLES COLLECTED ON 24 HOUR GLASS FIBER HIGH VOLUME FILTERS

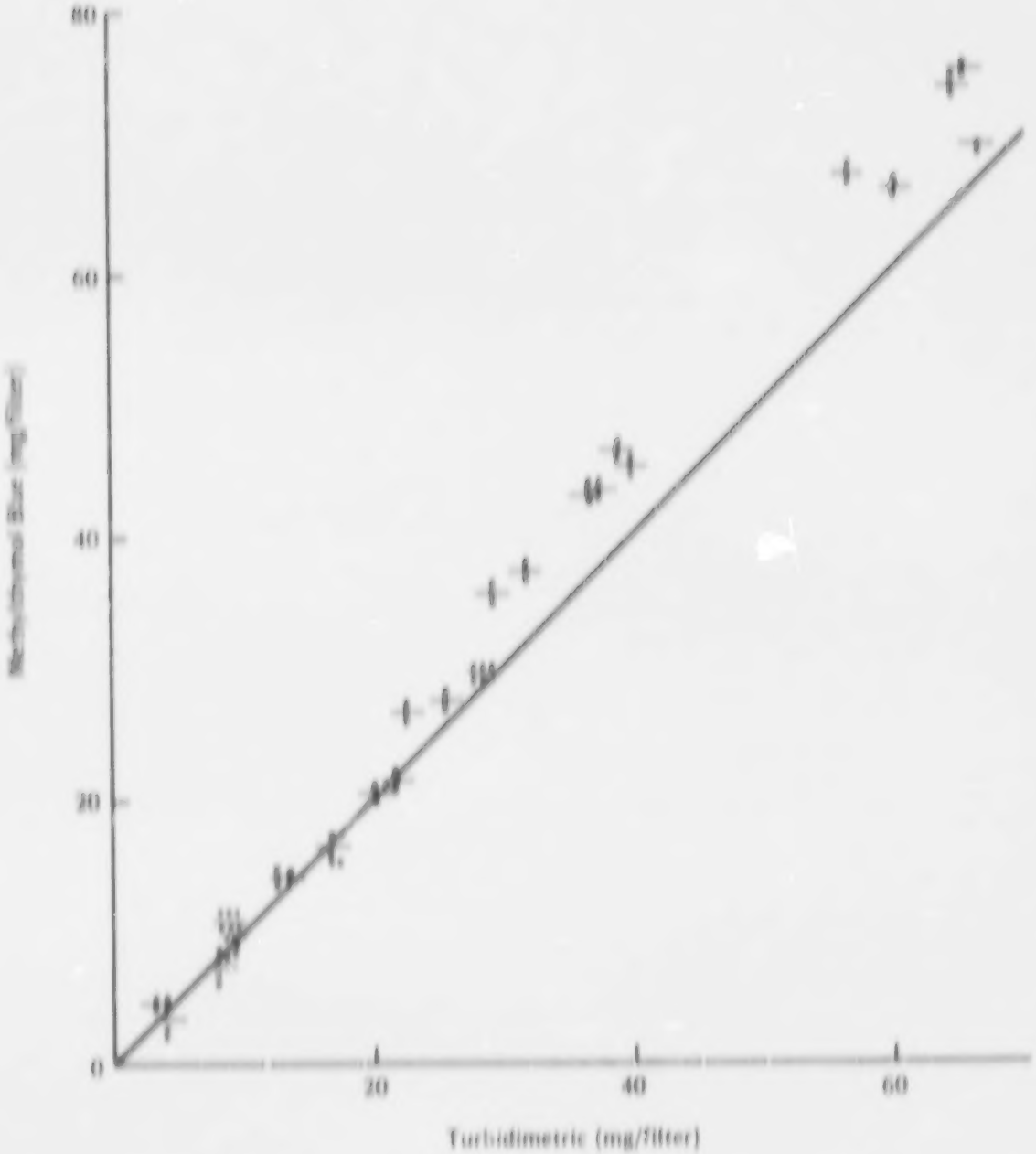


Figure 1

$SO_4^{=}$ + Ba-thorin dye → $BaSO_4$ + thorin dye complex

(a suspension) (a suspension)

The method can be carried out in several solvents. Procedures in both acetone and dioxane were evaluated in this study. The final medium containing 70% organic solvent, is necessary to reduce the dissociation of the Ba-thorin complex.

A comparison of the Brosset and AIHL microchemical methods for sulfate is shown in Table 2.

2. Dispensing Systems for Reagents and Samples

Several alternatives to the custom-made dispensing device of the original method were tried including the use of a diluting-dispensing syringe and a small volume reagent pipet all made by Lab-ding Industries. With this equipment, small variations in dispensed volumes caused a change in the ratio of sample to diluent and of reagent to diluent, which resulted in a change of the dissociation of the Ba-thorin complex and a shift in the absorption maxima. By employing dispensing pipets fabricated by Rainin, most of these variations were reduced significantly. The volume delivered by these dispensing pipets was shown to be within 1% of the nominal values. Employing the Rainin pipets the sample solution and the reagent mixture were measured independently. The diluent was added

Table 2

COMPARISON OF THE BROSSET AND MICRO AIHL METHODS FOR SULFATE

Brosset	Micro-AIHL
Ion exchange to avoid Ca, Pb, and other interferents.	Ca, Pb interferes only if in large amounts.
Sensitivity 0.1 to 0.2 μg/ml. Two ml of sample used.	Sensitivity 0.1 to 0.2 μg/ml. One ml of sample used.
Dioxane or acetone 70%, remainder water.	Acetonitrile 75%, remainder water.
Organic solvent used to reduce dissociation of Ba-thorin complex. The complex is a colloid which precipitates with time.	Organic solvent used to reduce solubility of $BaSO_4$ and increase rate. The Ba-nitrochromeazo complex is soluble and stable.
25 or 26 mm optical cell in sample beam. 520 to 480 nm filter or 520 nm monochromator, measuring decrease in absorbance. A single beam spectrophotometer is advised by C. Brosset. At AIHL a double beam instrument is used with a grey filter solution in the reference beam.	10 mm optical cell in reference beam. 642 nm in monochromator and double beam spectrophotometer necessary. A decrease of absorbance is measured.
Barium diluent contains 1% adipic acid to overcome H_2O_2 interference.	Not designed to work with solutions containing H_2O_2 (used for collection of SO_2).
Diluent is a 1:100 mixture of 0.21% $Ba(ClO_4)_2$ in 0.1 M $HClO_4$ and dioxane or acetone. 5 ml per test. Reagent is a 0.0025% thorin solution in 0.001 N H_2SO_4. 0.125 ml per test (6.125 μg SO_4 added per test).	Diluent-reagent mixture is a 2:100 mixture of 0.001 M $BaCl_2$ with 85% acetonitrile, containing 0.12% pyridine, 0.12% benzenesulfonic acid, 0.00375% nitrochromeazo. 8 ml per test.
Total volume 7.125 ml containing 312 μg thorin.	Total volume 9.0 ml containing 300 μg nitrochromeazo.
Ba concentration 6.25×10^{-5} M in diluent. 0.312 μM Ba per test. 0.064 μM SO_4 per test.	Ba concentration 2×10^{-5} M in reagent. 0.160 μM Ba per test.
Approximate working range 2 to 9 μg/ml.	Range 5 to 14 μg/ml.

with a repetitive dispensing syringe. The reagent mixture contains sufficient sulfate to react with 20% of the barium contained in the diluent to repress the solubility of $BaSO_4$ and promote rapid equilibrium.

3. Ion Exchange Treatment of Samples

The function of the ion exchange paper is to remove cations which might interfere in the determination; metal ions are replaced by H^+. To obviate the use of inconvenient ion exchange columns as suggested in the original method, discs were punched from ion exchange paper and inserted into disposable plastic syringe bodies for use.

The degree of removal of sodium ion by filter discs was used to establish the efficiency of the system. The sample solution was filled in to the syringe bodies and allowed to drip slowly through the tip into small beakers. Flame photometric determinations were used to monitor the extent of sodium penetration. With one filter disc, penetration was evident. It was eliminated by employing two filter discs in series. For added security three filter discs were used routinely.

4. Drifting of Reagent Blank Spectrophotometer Value

During use of a double beam Bausch and Lomb UV 200 Spectrophotometer it became evident that the reagent blank plus excess sulfate placed in the reference beam of the instrument caused drifting. This drifting could be prevented by filling the reference beam cell with a gray filter solution. A gray filter solution was prepared with $CoSO_4$, $CuSO_4$ and $NiCl_2$ which gave a reasonable flat absorbance between 440 and 540 nm.

5. The Influence of Sodium on Analytical Precision

As summarized in Tables 3 and 4 a comparison was made between sulfuric acid and sodium sulfate standards to assess the influence of sodium on analytical precision (without ion exchange). The comparison was made with both acetone and dioxane as solvents. In both cases the sodium sulfate standards yielded somewhat better precision. The influence of cell size on precision can also be examined with both sulfate reagents. No clear trend is evident so we infer that the precision with these reagents is approximately equal for both cell lengths.

6. Precision of the Modified Brossett Procedure with Ion Exchange Treatment

Table 5 lists the coefficients of variation (C.V.) for four replica-

Table 1: COMPARISON OF H_2SO_4 AND $NaHSO_4$ STANDARDS IN ANALYSIS BY THE MODIFIED BROOKS PROCEDURE (In acetone) WITH 2.5 and 5.0 cm CELLS WITHOUT ION EXCHANGE

Reagent	Number of Experiments[a]	Cell length, cm	Coef. of Variation %
H_2SO_4	1	2.5	5.5
Na_2SO_4	2	2.5	3.0
H_2SO_4	2	5.0	4.7
Na_2SO_4	1	5.0	4.0

[a] Each experiment includes three replications at each of five concentrations, 2,4,6,8 and 10 μg/ml $SO_4^=$.

Table 4 PRECISION[a] OF H_2SO_4 AND Na_2SO_4 STANDARDS IN "DIRECT ANALYSIS" BY THE BROBST PROCEDURE IN DIOXANE[b]

	μg/ml Sulfate[c]					
Reagent	2	4	6	8	10	Overall
Na_2SO_4	5.1	6.4	7.5	8.7	8.1	4.5%
H_2SO_4	17.3	8.9	4.4	8.1	8.3	9.8%

a. Expressed as coefficient of variation of four replications at each concentration.

b. "Direct Analysis" indicates no ion exchange treatment.

c. The true concentrations with the Na_2SO_4 standards are within 1% of the nominal concentrations shown. The H_2SO_4 standards are consistently lower by 4% than the nominal values shown.

Table 5 PRECISION[a] OF THE MODIFIED BROBST PROCEDURE WITH ION EXCHANGE TREATMENT (three filter discs)[b]

	µg/ml Sulfate[c]					
Solvent	2	4	6	8	10	Overall
Acetone	4.3	5.0	2.8	0.9	0.8	2.2%
Dioxane	11.3	1.9	5.1	2.9	2.6	3.9%

a. Expressed as coefficient of variation of four replications at each concentration.

b. Pretreatment of filter discs was the same in all cases; filter discs were soaked in distilled H_2O for several hours then drained and dried overnight in a stream of clean air.

c. The true concentrations are within 1% of the nominal values shown and employed Na_2SO_4 as the sulfate source.

tions at each of five sulfate concentrations employing standard sulfate solutions and ion exchange. In both acetone and dioxane, C.V. values generally decreased with increasing concentration of sulfate, with dioxane results usually less precise than those in acetone.

7. Recovery of Sulfate by a Modified Brosset Procedure with Ion Exchange Treatment

Table 6 summarizes results for recovery experiments with four replications at each of five sulfate levels in both acetone and dioxane. Percent recoveries after ion exchange are calculated relative to direct determination without such pretreatment. Recoveries were generally slightly in excess of 100% with particularly large apparent sulfate pickup at the lowest standard solution level. Since most samples to be analysed are expected to be in the 4-10 µg/ml range the recoveries shown, ranging from 96 to 113% are considered adequate. Acetone results appear to be somewhat better than those in dioxane.

8. Conclusions

The acetone modification of the Brosset procedure with three pretreated ion exchange filter discs will be the one used for the remainder of this test. The protocol followed is given in Appendix D.

Table 6: RECOVERY[a] OF SULFATE BY MODIFIED BROQUET AFTER TREATMENT WITH ION EXCHANGE FILTER DISCS[b]

	µg/ml Sulfate					
Solvent	2	4	6	8	10	OVERALL
Acetone	113 ± 27	96 ± 9	104 ± 6	100 ± 3	104 ± 3	103% ± 1
Dioxane	136 ± 7	113 ± 4	110 ± 5	103 ± [illegible]	101 ± [illegible]	107% ± [illegible]

a. Expressed as a percent of sulfate determined by direct analysis without ion exchange treatment.

b. Pretreatment of filter discs as in footnote b, Table 5.

c. Same as footnote c, Table 5.

IV. THE EFFECTS OF INTERFERENTS ON SULFATE DETERMINATIONS

A. Description of the Experiments.

The experimental design calls for an evaluation of the influence of a series of potential interferents including:

a. sulfide
b. sulfite
c. persulfate
d. sulfur
e. phosphate
f. lead sulfate
g. calcium
h. lead

Based upon a more detailed evaluation of the interferences most likely to be significant, the above list was modified and lengthened to the following 12:

Anionic	Parent Compound
sulfide	1:1 $Na_2S \cdot 9H_2O$:NaOH
sulfite	$NaHSO_3$
persulfate	$K_2S_2O_8$
thiosulfate	$Na_2S_2O_3$
bicarbonate	$NaHCO_3$
phosphate	$Na_2HPO_4 \cdot 12\ H_2O$
silicate	$Na_2SiO_3 \cdot 9H_2O$

Cationic	Parent Compound
barium	$BaCl_2 \cdot 2H_2O$
calcium	$CaCO_3$ + acetic acid
lead	$Pb(NO_3)_2$

Other	
colloidal clay	Kaolinite
p-benzoquinone	---

The interferents eliminated from this evaluation include elemental sulfur and lead sulfate. p-benzoquinone, was included to simulate the yellow chromophores present in some aqueous extracts of atmospheric particulate matter. Bicarbonate and silicate were added because these are thought to be found in aqueous extracts from glass fiber filters together with ions such as Na^{+} and Ca^{+2}. Thiosulfate was included because it is an end product of the reaction of sulfur and sulfite as well as being produced during oxidation of many reduced sulfur species under alkaline conditions. Finally, colloidal clay was added since it may be easily obtained in filtered extracts from atmospheric particulate matter.

It is recognized that interference effects relatable to the cationic potential interferents may result from interactions with sulfate during the sampling, extraction or analysis phase. However, the determination of the point at which interference, if any, occurs was beyond the scope of this study.

For turbidimetry and the NTB methods the interferents were examined at the concentration levels 10 µg/ml and 30 µg/ml, at each of two sulfate levels, zero and 20 µg/ml. Where significant interference was found, an evaluation at 60 µg/ml of sulfate was also done. With the modified Brosset and AIHL microchemical procedures the restricted range of the methods required dilution of these concentrations by a factor of 2.5. Thus interferents were actually evaluated with these methods at 4 and 12 µg/ml levels with 0 and 8 µg/ml sulfate. For ease in comparison of findings, all results with the latter two methods were then multiplied by 2.5.

Replicated data are distinguished by the quotation of the experimental precision found (i.e. ± 1σ). Other data presented were the result of a single trial. Separate experiments established the time dependence with unstable interferents.

B. Results of Interference Studies

The effects of the interferents have been expressed as "µg/ml observed sulfate". Tables 7, 8, 9, 10 and 11 summarize such data for the interferents studied with the four wet chemical methods. Data for the Brosset procedure were obtained with both acetone and dioxane modifications.

Tabulation and comparison of results for sulfide and sulfite are com-

Table 7: Interference Effect with Turbidimetric Method (μg/ml Observed Sulfate)

Sulfate level, μg/ml	0		20		60	
Interferent level, μg/ml	10	30	10	30	10	30
Interferent						
Sulfide	13	20	26[b]	51[b]	80	91
Sulfite	25	31	33[c]	52[c]	74	95
Phosphate	2.8	~2.5			62	60
Colloidal clay	<1.0	3.3	5.0	30	58	60
Bentonite	2.8	6.9	21	27	nd[a]	nd
Chromate	~1.0 to 1.5	<1	27	27	nd	nd
Bicarbonate	<1.0	~2.5	22	29	nd	nd
Silicate	~1.0 to 1.5	2.8	21	29	nd	nd
p-Nitrophenolate	<1.0	<1	20	29	nd	nd
Borate	~1.0 to 1.5	<1	14	3	nd	nd
Chloride	3.0	~2.5	20	21	nd	nd
Lead	<1.0	<1	22	21	nd	nd

a) Not determined

b) Repetition of these experiments with fresh (i.e. < 3 hours old) dilute sulfide-sulfate solutions yielded 25 ± .3 and 25 ± 1.2 for 10 and 30 μg/ml sulfide, respectively. Comparison of results indicate substantial aging for the solutions employed here. See Table 12.

c) Repetition of these experiments with fresh (i.e. < 3 hours old) dilute sulfite-sulfate solutions yielded 21.5 ± .1 and 21.8 ± 1.0 and 30 μg/ml sulfite, respectively. Comparison of results indicate substantial aging for the solutions employed here. See Table 12.

Table 9: Interference Effect with AIDS Biochemical Method (μg/ml Observed Sulfide)

Actual sulfide level, μg/ml	0		20	
Interferent level, μg/ml	10	30	10	30
Interferent				
Sulfide	1.7	14	25[a]	36[a]
Sulfite	0.2	23	29[b]	33[b]
Phosphate	<0.5	<0.6	20.0 ± .1	20.5 ± 0
Colloidal clay	<0.5	<0.6	8	30
Bentonite	5.0	11	27	32
Chromium	<0.5	<0.6	21	22
Diethanol	<0.5	<0.6	19	19
Silicate	<0.5	<0.6	19	19
p-Nitrophenol	<0.5	<0.6	19	19
Barium	<0.5	<0.6	11	<0
Calcium	<0.5	<0.6	16	11
Lead	<0.5	<0.6	14	6

[a] Repetition of these experiments with fresh (i.e. < 3 hours old) dilute sulfide-sulfate solutions yielded 21.4 ± .1 and 35 ± 2 for 10 and 30 μg/ml sulfide, respectively. Comparison of results indicates substantial aging for the solutions employed here. See Table 12.

[b] Repetition of these experiments with fresh (i.e. < 3 hours old) dilute sulfite-sulfate solutions yielded 25.8 ± .4 and 38.4 ± .2 for 10 and 30 μg/ml sulfite, respectively.

Table II: Interference Effect with the Modified Brezner Method, in Acetone (µg/ml Observed Sulfite)[a]

Actual Sulfite level, µg/ml	0		20	
Interferent level, µg/ml	10	30	10	30
Interferent				
Sulfide[b]	0.8 ± .5	0.6 ± .1	20 ± 1	23 ± 4
Sulfite[b]	3.7 ± .4	7.9 ± .1	23 ± 1	28 ± .2
Phosphate	< 0.2	< 0.2	20 ± 1.6	19 ± 0.9
Colloidal clay	< 0.2	< 1.0	18 ± .3	19 ± .3
Bromide	1.2 ± .04	2.5 ± .1	19 ± .3	21 ± .1
Chloride	1.5 ± 1	1.8 ± .5	20 ± .4	22 ± .1
Bicarbonate	< 0.2	< 5	19 ± .5	18 ± .8
Silicate	< 0.5	< 0.8	19 ± .7	20 ± 1.6
p-benzoquinone	< 0.2	< 0.2	18 ± .5	20 ± .4
Calcium	0.6 ± .1	1.8 ± .8	19 ± .1	19 ± .3
Lead	2.2 ± .2	4.5 ± .1	19 ± .4	19 ± .1

[a] See footnote a, Table II.

[b] Results above are means for trials conducted with fresh solutions (i.e. about 1 hour old). Results are highly dependent on aging time.

Table II: Interference Effect with the Modified Brower Method, in Micrograms (μg/ml Observed Sulfide)[a]

Actual Sulfide level, μg/ml	0		20	
Interferent level, μg/ml	10	30	10	30
Interferent				
Nitrite[b]	2 ± .7	2 ± .7	21 ± 1.3	25 ± 5
Sulfite[b]	4 ± .6	11 ± .5	24 ± 2.5	> 29
Phosphate	1.2 ± .3	1.6 ± .2	19 ± 1.6	19 ± 1
Colloidal clay	< 0.7	1.2 ± .2	18 ± 1	20 ± .4
Fluoride	2 ± .4	4 ± .3	20 ± .5	20 ± .6
Chloride	1 ± .7	5 ± .4	21 ± .6	24 ± .2
Bicarbonate	< 1	< 0.6	21 ± .4	20 ± .5
Silicate	< 0.5	< 0.8	19 ± .7	19 ± .6
p-Phenolphthene	2 ± .7	< 0.6	20 ± .5	21 ± .6
Chloride	< 0.5	< 0.8	19 ± .5	19 ± 1
Lead	< 0.8	< 1	19 ± .8	20 ± .9

[a]The Brower method cannot be used above or 10 μg/ml $SO_4^{=}$ without dilution. As with the ASTM method all studies were done after diluting by a factor of 2.5. Thus the sulfide levels in the solutions analyzed were 0 and 8 μg/ml and the interference levels, 4 and 12 μg/ml.

[b]Results shown are means for trials conducted with fresh solutions (i.e. about 1 hour old). Results are highly dependent on aging time.

plicated by significant aging effects. Results for fresh solutions of these anions were generally available only with up to 20 μg/ml sulfate since 60 μg/ml sulfate greatly exceeded the range for two of the four methods. Thus for internal consistency the results tabulated are with solutions of the same but indeterminate age. Values for fresh solutions of these anions are listed by footnotes in these tables.

The laboratory data from these interference studies can be displayed in a format which may be termed an "Interferogram" (Figure 2). The interferogram is based upon the standard working curve of sulfate absorbance vs. sulfate concentration. In the example the influence of interferents at 30 μg/ml with sulfate at 20 μg/ml is shown with the AIHL microchemical method. Since an 0.4 ml sample aliquot is diluted to 1.0 ml as part of the analytical procedure, the concentrations shown on the ordinate are lower than the above by a factor of 2.5.

The true concentration of sulfate, C_0, is noted by the vertical line. Horizontal lines, labelled t_x represent a given interferent, are plotted at the absorbance found with the added interferent. For interferent y the intersection of the horizontal line with the working curve is the apparent sulfate level, C_y. The interference effect, in μg/ml apparent $SO_4^=$, is given by C_y-C_0 and may be either positive or negative as shown by the s-shaped pattern. For a given sulfate level and method, the interferogram provides a graphical ranking of interferents by sign and magnitude.

Interferogram for AIHL Microchemical Method

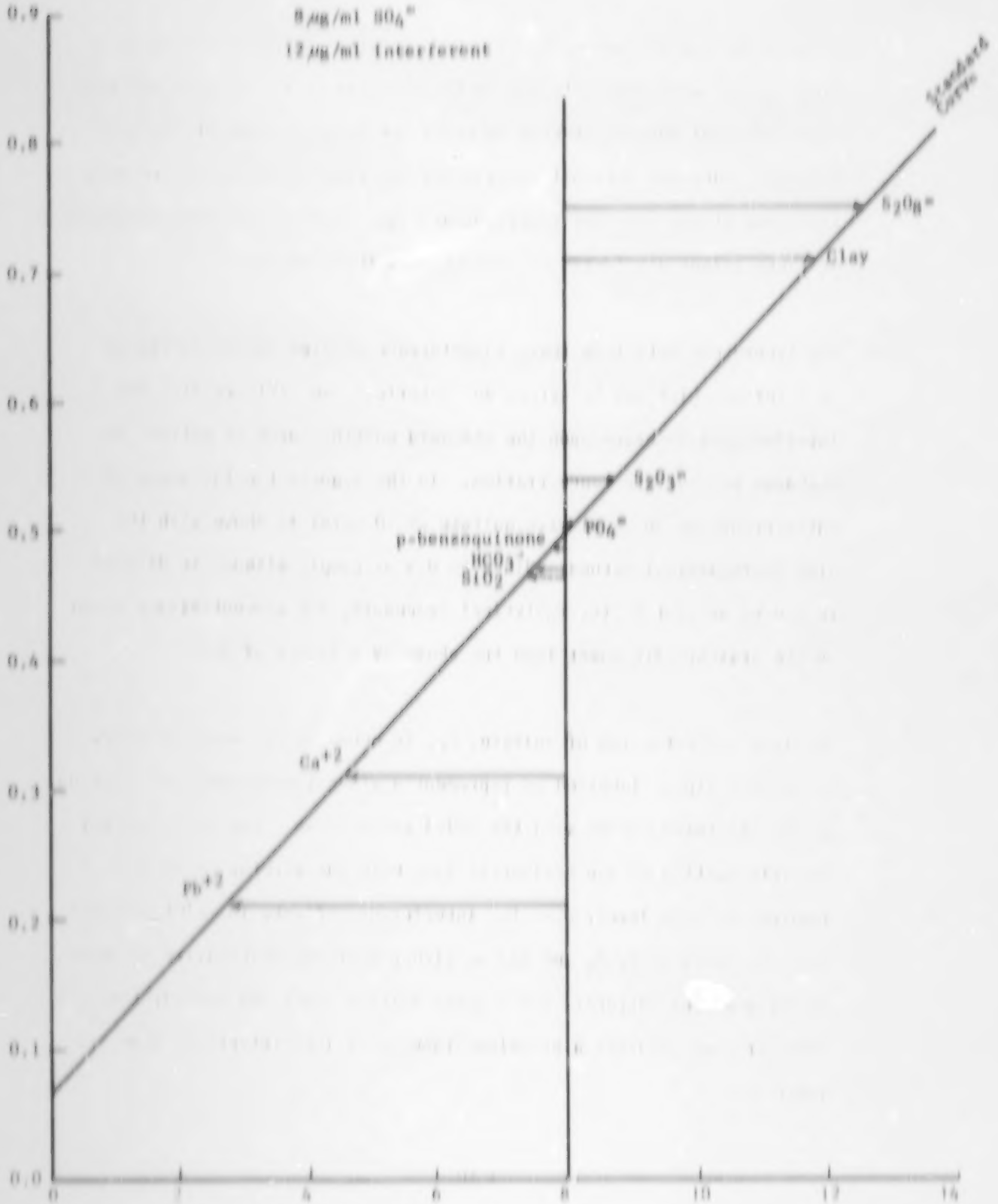


Figure 2

interferograms are included as figures 2 through 8. Results for the unstable anions sulfide and sulfite are not shown in the figures because of the time dependence of their interference effects. In figures 5 and 6, the working curve over the range 0-60 µg/ml sulfate has been approximated as a straight line. In fact it is slightly "S" shaped with very marked deviations from linearity above ca. 60 µg/ml. Since for figures 7 and 8 apparent sulfate levels above 60 µg/ml are measured the working curve extends to 80 µg/ml. In representing this as a continuous function the more precise characterization of the working curve below 60 µg/ml is shown.[6]

C. Time Dependence of Interference Effects with Unstable Anions

Two independent experiments were conducted to explore the influence of aging of dilute sulfate-interferent solutions with sulfide, sulfite, thiosulfate and persulfate. The first employed only one method, the modified Brosset procedure (in dioxane) with the four interferents at 0 and 20 µg/ml sulfate. The second employed all four methods (with both the acetone and dioxane variations of the Brosset procedure) with the two most unstable interferents at 20 µg/ml sulfate.

[6] In section IVC, results obtained by linear regression in the 0-60 µg/ml range are compared to those using a 3rd order polynomial to fit the S-shaped function.

Interferogram for $BaCl_2$ Turbidimetric Method

20μg/ml $SO_4^=$

10μg/ml Interferent

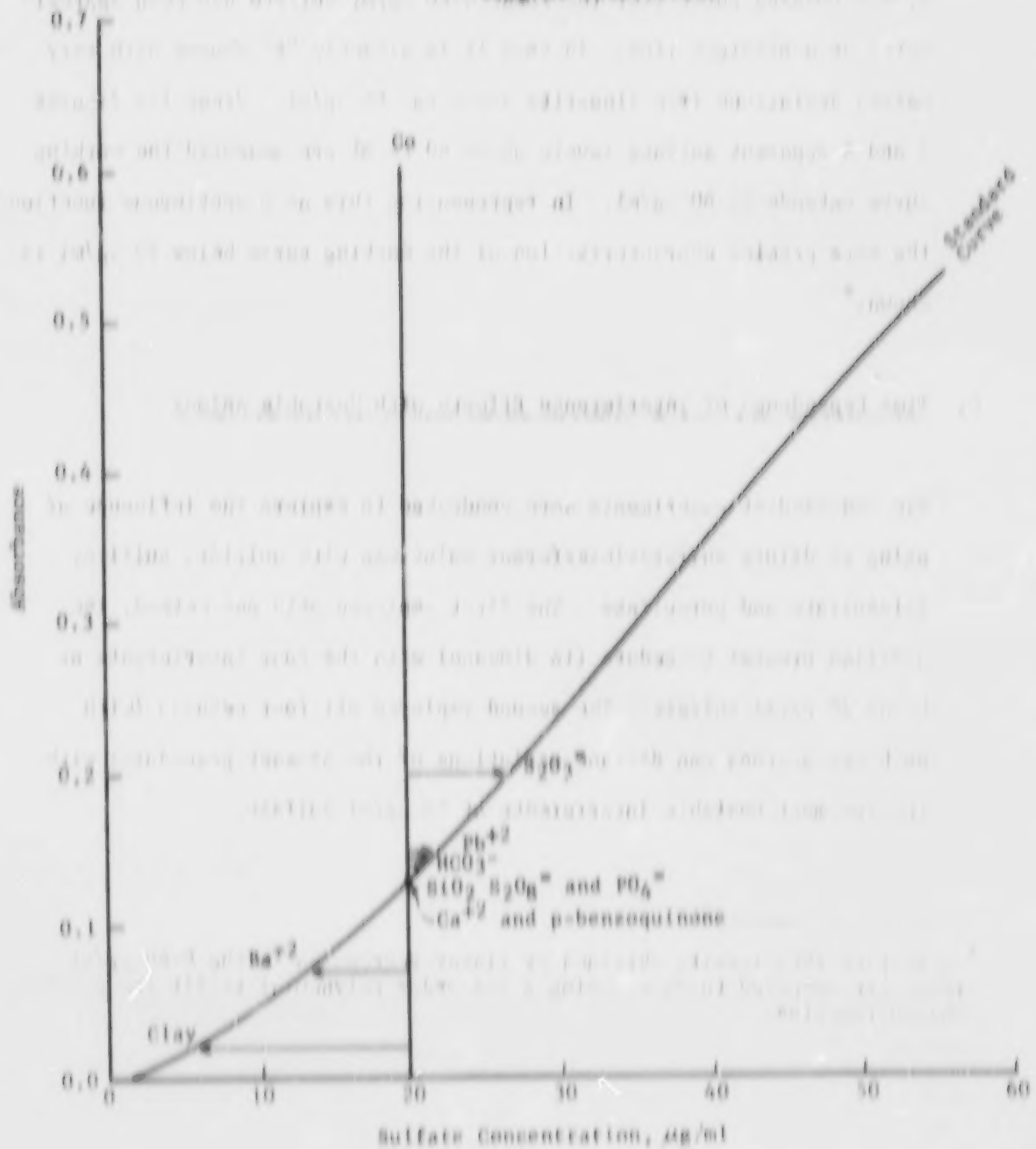


Figure 3

Interferogram for $BaCl_2$ Turbidimetric Method

20μg/ml $SO_4^=$

30μg/ml Interferent

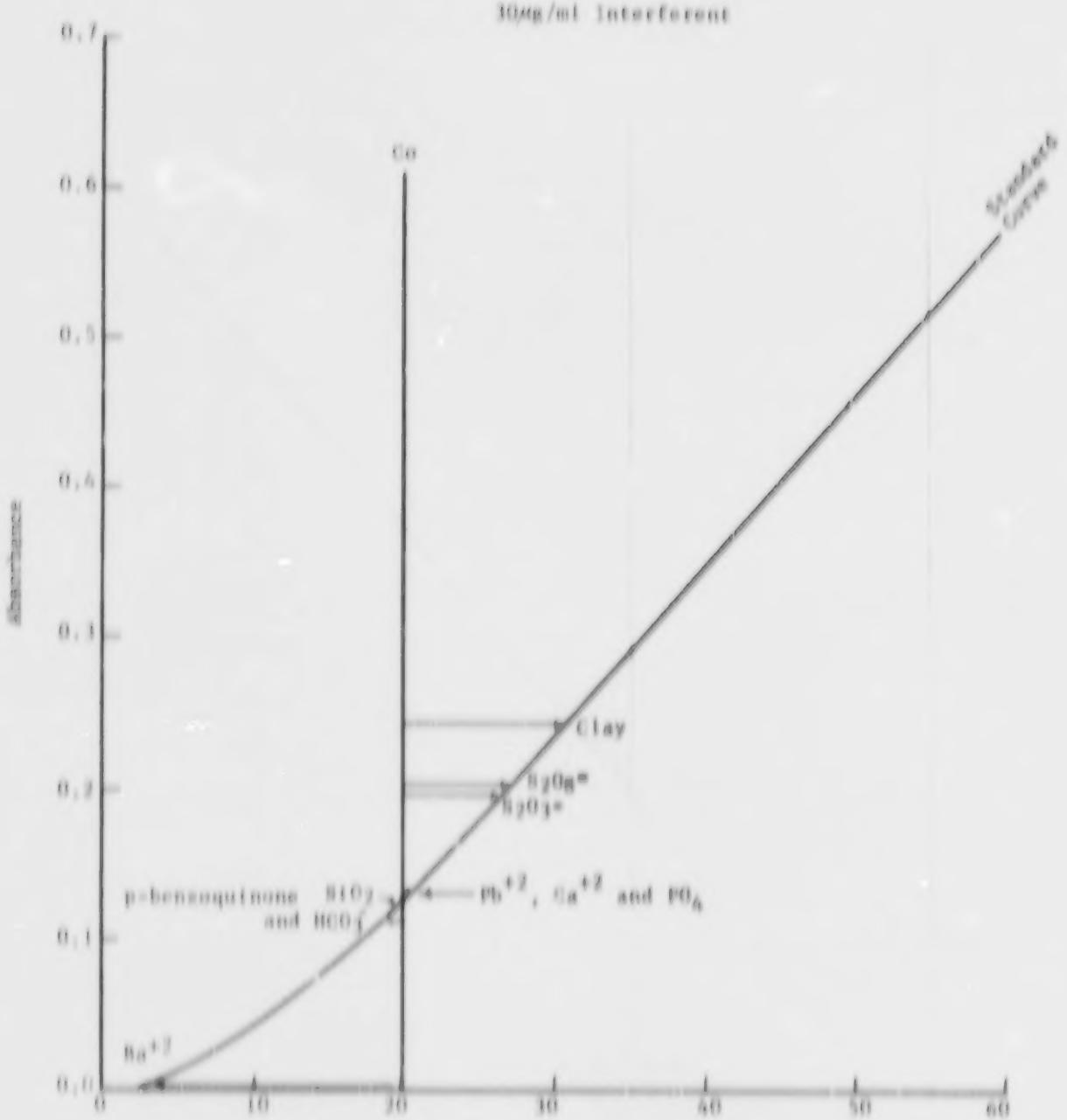


Figure 4

Interferogram for Methylthymol Blue Method

20µg/ml $SO_4^{=}$

10µg/ml Interferent

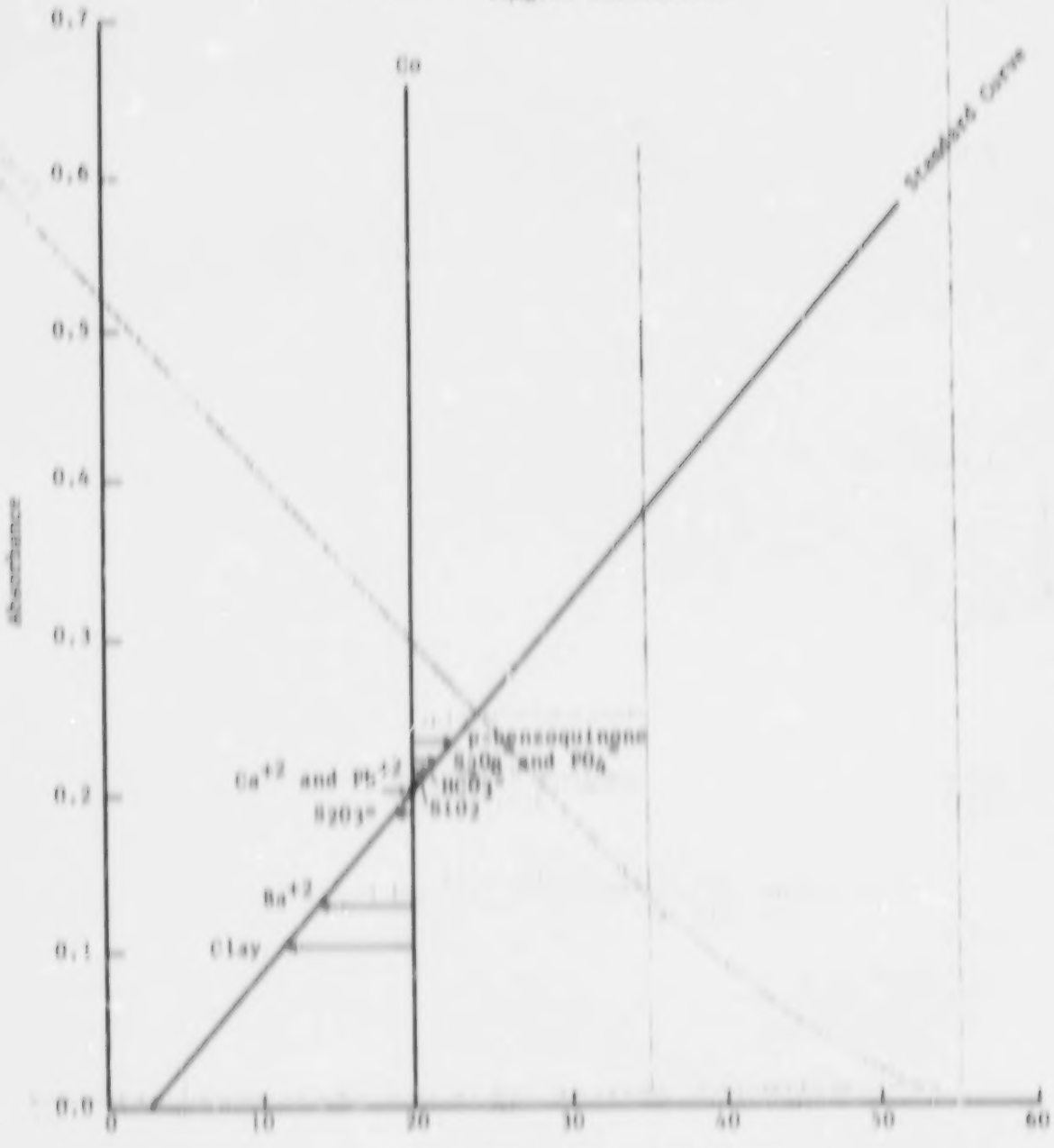


Figure 5

Interferogram for Methylthymol Blue Method

20ug/ml $SO_4^{=}$

30ug/ml interferent

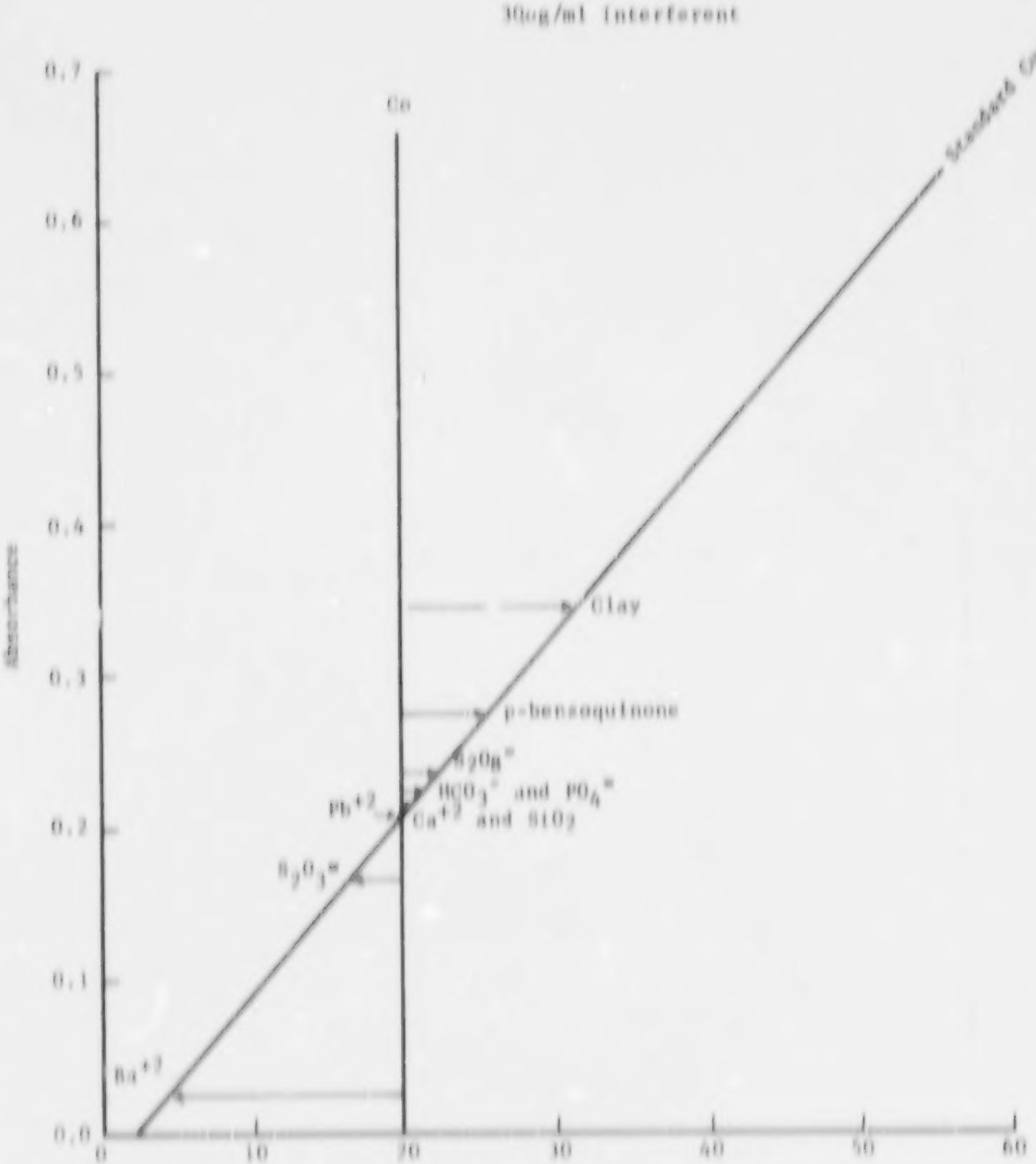


Figure 6

Interferogram for Methylthymol Blue Method

60μg/ml $SO_4^{=}$

10μg/ml Interferent

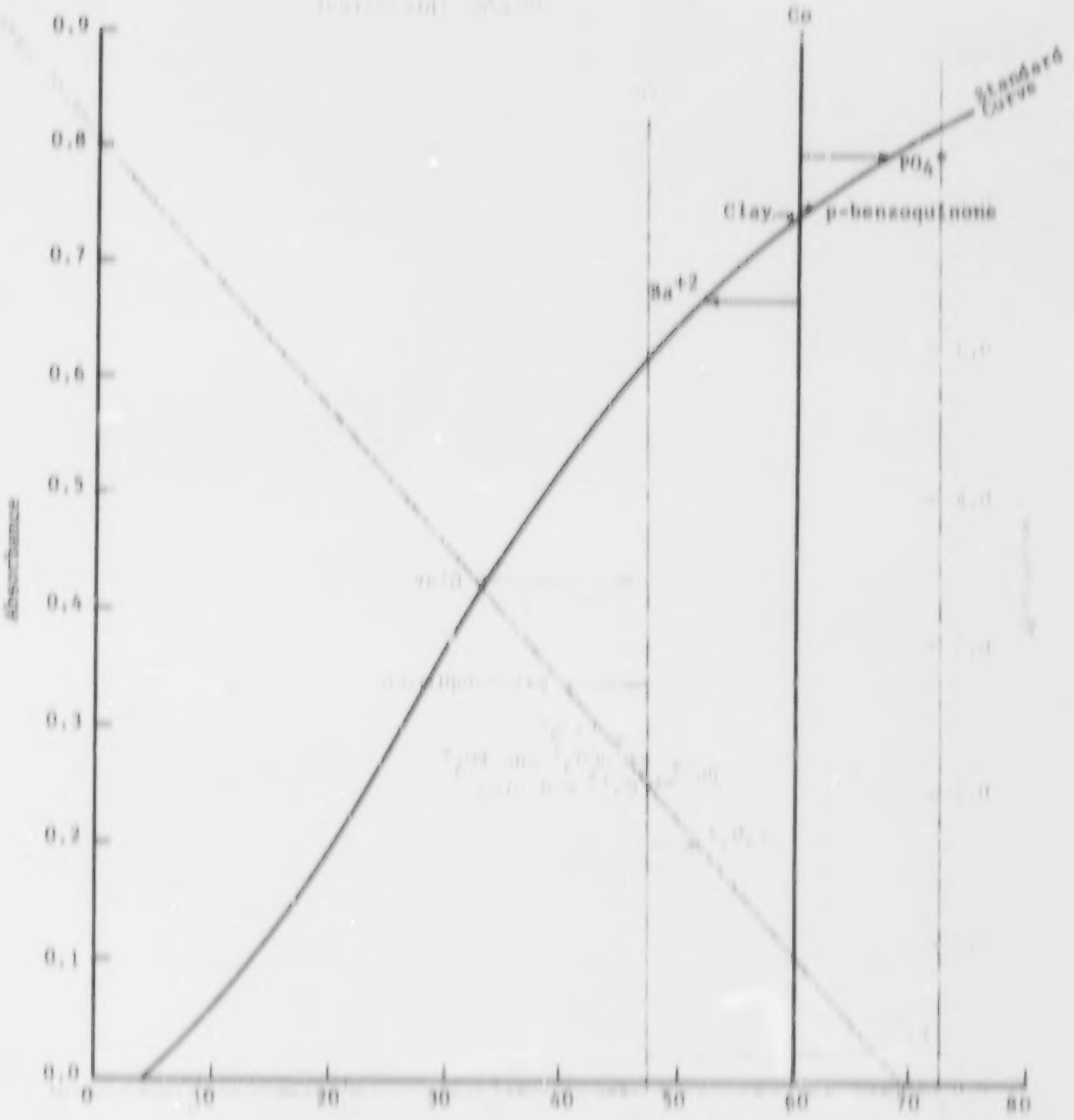


Figure 7

Interferogram for Methylthymol Blue Method

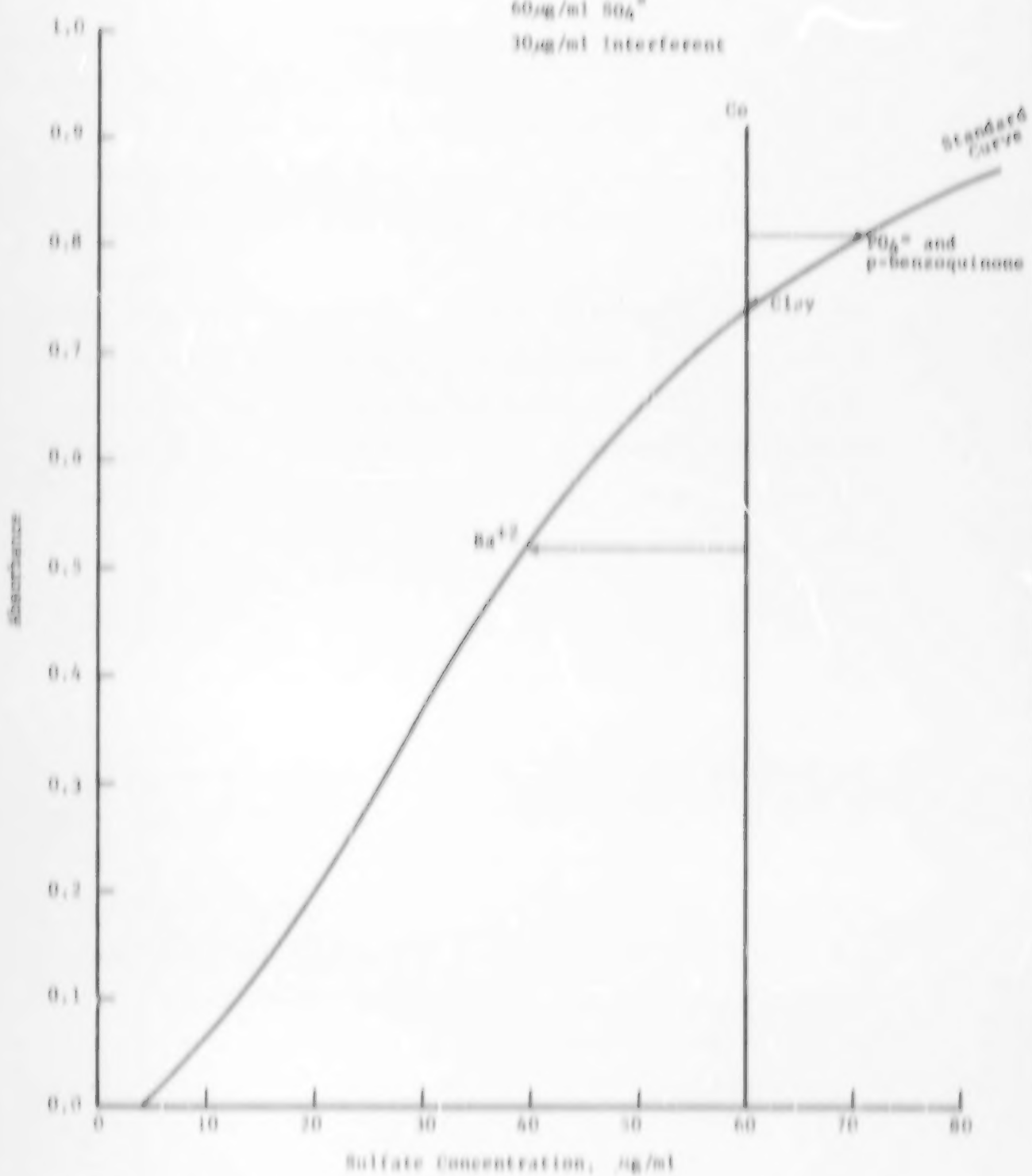


Figure 8

Results of the study using the modified Brossat method with four interferents are shown in Table 12. In all cases the interference is positive with increasing effects with time. Comparing solutions with and without sulfate, the effects of sulfide, thiosulfate and sulfite appear to be independent of the presence of sulfate. Note that the measured sulfate in the presence of $S^{=}$ and $SO_3^{=}$ exceeded the range of the method after extended storage periods. Assuming complete oxidation to sulfate, 30 µg/ml of $S^{=}$ is theoretically capable of generating 90 µg/ml of $SO_4^{=}$, and 30 µg/ml of $SO_3^{=}$, 36 µg/ml of $SO_4^{=}$. Initial interference effects and changes with time for sulfate-thiosulfate and sulfate-persulfate were relatively small compared to those for sulfide. While sulfite appears to undergo only modest increases (where measurable) this reflects, in part, the apparently rapid oxidation occurring in the first hour before analysis.

Based upon these findings, studies with the four methods employed only sulfide and sulfite. With these two interferents, the results have been calculated using four replications for the MTB method and two replications each for the other three methods. Sulfide time dependence results are shown in Table 13. The results with the modified Brossat method (in dioxane) for fresh solutions are substantially different from those in Table 12. For example, 28 ± .4 µg/ml observed sulfate with 30 µg/ml sulfide added to 20 µg/ml sulfate compares to 21 ± .9 reported in Table 12. These findings imply very marked aging effects occurring within one hour of solution preparation, making reproducibility

Table 12: The Effect of Aging of Interference-Sulfide Solutions on Interference Effects by the Modified Brewer Method (in dioxane)

Sulfide level, µg/ml	0						20					
Time, hours	0-5[a]		70-75		500-550		0-5[a]		70-75		500-550	
Interference levels, µg/ml	10	30	10	30	10	30	10	30	10	30	10	30
Interference												
Sulfide	2 ± .7	2 ± .7	9 ± .4	25 ± .3	> 30°	> 30°	20 ± .5	21 ± .9	28 ± .2	29 ± 1	> 30°	> 30°
Thiosulfate	1 ± .7	5 ± .4	100[b]	100	3 ± .7	7 ± .5	21 ± .6	24 ± .2	100	100	23 ± .8	27 ± .2
Persulfate	2 ± .4	4 ± .3	100	100	7 ± .3	11 ± .4	20 ± .5	20 ± .8	100	100	24 ± .6	27 ± .4
Sulfite	4 ± .6	11 ± .5	9 ± .5	16 ± .2	12 ± .3	> 30°	23 ± .9	28 ± .2	27 ± .3	>30°	28 ± .7	> 30°

[a] Have exact solution ages: Sulfide 0.5 hours
Sulfite 1.0
Thiosulfate 5.0
Persulfate 5.0

[b] Not determined.

[c] Range of method exceeded.

Table 13: The effect of aging of sulfide-sulfate solutions on interference effects by four methods (20 µg/ml added sulfate)

Method		ASE, Micro[b]		Brucaet, acetone[b]		Brucaet, chromic[b]		Turbidimetric		Technicon AA II[b]	
Sulfide level µg/ml		10	30	10	30	10	30	10	30	10	30
Observed $SO_4^{=}$	µg/ml	21.4	28.8	20.6	25.6	21.5	28.0	22.8	25.4	18.3	20.5
0-3 hours[c]	σ	.1	2.1	.1	.1	.4	.4	.3	1.2	2.7	1.3
Observed $SO_4^{=}$	µg/ml	30.8	35.6	28.6	29.2	> 30	> 30	31.6	54.0	27.3	37.6
48 hours	σ	.1	.2	.2	.2	—	—	.4	.9	.7	4.6

[b]Data reduction by linear regression

[b]See Table II, footnote a

[c]Here exact solution age at time of analysis: ASE alone: 1 hour
Brucaet (both modifications): 1
Turbidimetric: 1
AA II: 3

difficult. The interferents effects tabulated for sulfide in Table 11 at 20 $\mu g/ml$ are the means of results for the 0-1 hour old solutions reported in Table 12 and 13.

Of the four methods with aged sulfate-sulfide solutions the modified Brosset method in acetone and the MTB procedure yielded the least interference effects with aged sulfate-sulfide solutions. The greatest interferences was found with the turbidimetric method.

The results for sulfite are shown in Table 14. Comparing these results to those in Tables 7-9 reveals generally similar findings. However, the present data indicate that the AIHL microchemical method is subject to the greatest interference effect by sulfite whereas previously this was observed for the turbidimetric method. The MTB method demonstrated the least interference effect by sulfite.

Finally, comparing aged solutions of sulfide and sulfite with sulfate, greater interference was found with sulfide. The generally smaller changes between 0-3 and 48 hours for sulfite, and the quite substantial initial interference effects suggest faster oxidation of sulfite to sulfate than is found with sulfide.

D. Recommendations to Eliminate Interferences

The methods used in the present study are affected by interferents

Table 14: The effect of aging of sulfite-sulfate solutions on interference effects by four methods (20 μg/ml added sulfite)

Method		AIHL Micro[b]		Brosset, acetone[b]		Brosset, dioxane[b]		Turbidimetric		Indophenol WSP[b]	
Sulfite level μg/ml		10	30	10	30	10	30	10	30	10	30
Observed $SO_4^=$	μg/ml	26.8	38.4	21.8	27.7	26.0	> 30	21.5	21.8	21.1	24.2
0-3 hours[c]	σ	.4	.2	.4	.1	1.1	—	.1	.5	.5	1.0
Observed $SO_4^=$	μg/ml	28.9	39.4	26.0	29.0	27.8	> 30	25.2	34.6	23.4	34.7
4d hours	σ	.3	.1	.1	.1	.8	—	.1	.4	.4	.6

[b] Data reduction by linear regression

[b] See Table II, footnote a

[c] Here exact solution age at time of analysis: AIHL micro: 1 hour
Brosset (both additions): 1
Turbidimetric: 1
WSP: 3

extracted from both the filters and particulate matter samples. As previously demonstrated these interferents may affect the results from the four methods quite differently. In the following, possible means to overcome interference will be discussed.

1. Turbidimetric Method

Because of the substantial sample requirement (e.g. ≥ ca. 20 ml of 20 µg/ml sulfate), high volume samples are usually necessary to permit use of this method. Filter materials commonly available for this purpose are glass fiber and cellulose. Preliminary findings indicate that glass fiber filters release substantial amounts of soluble silica which, upon subsequent acidification and addition of $BaCl_2$, co-precipitates with the $BaSO_4$ as silicate and acts as a nucleating agent. As a result the apparent blank sulfate value for a glass fiber filter may be anomalously high. Furthermore we believe such apparent blank values to be dependent on the total sulfate in the extract, the apparent sulfate ascribable to the filter decreasing with increasing total sulfate. Therefore, calibration curves for sulfate determination for samples collected with glass fiber filters should be made using blank filter extracts for making up the calibrating solutions.

2. MIR Method

The bright methylthymol blue-Ba complex, upon reacting with sulfate in alkaline solution, splits off the grayish methylthymol blue dye and forms a suspension of $BaSO_4$. The positive absorbance shift at 460 nm (orange region of the spectrum) is used for quantitation of sulfate. Since many atmospheric particle extracts contain substances absorbing appreciably at this wavelength, especially at higher values of pH, this produces a positive interference. The significance of this effect was evaluated, as discussed in Section II A4, for a group of samples from Riverside, California. In this case this interference represented less than one percent of the observed sulfate. Thus it is unclear if this source of interference would be sufficient to warrant correction. With strongly absorbing extracts, such interference could be eliminated by using a dual channel Technicon system replacing the reagent by a colorless solvent, e.g. BuT alcohol, in one channel or by subtracting blank values obtained in a subsequent run of a single channel instrument, without the reagent.

3. AIHL Microchemical Method

This method is significantly affected by calcium at levels found in particulate matter extracts. It was found that this interferance, could be eliminated using two approaches: ion-exchange paper discs,

as in the modified Brosset method or addition of citric acid to the reagent solution (≈ 0.3 g/liter). With the latter approach, ratios of $Ca^{++}/SO_4^{=}$ up to 4 could be tolerated with only a slight loss in accuracy. No loss was experienced up to a ratio of one. The inconvenience of the long reaction time (30 min. to an hour) can be reduced to 10 min. by forming a suspension of $BaSO_4$ corresponding to 1 µg/ml in the reagent. The reagent containing both corrections extends the range from the present 6-12 to 1-14 µg of sulfate.

4. Modified Brosset Method

The AIHL modification of this procedure employing paper discs coated with ion exchange resin has significantly simplified the method and reduced the sample requirement. Nevertheless, the sample volume needed remains relatively high (ca. 3 ml) compared to a maximum of 1 ml with the AIHL method.

The only significant interferents are sulfur-containing anions. Techniques for reducing the influence of these interferents have not been investigated.

E. Summary and Conclusions

Based upon the interference study data the following observations are made:

1. The modified Brosset method is the technique least subject to interference effects with the interferents studied.

2. Sulfide and sulfite are generally strong positive interferents with all of the methods studied. While very fresh solutions of these anions with sulfate display reduced effects, these conditions are considered unlikely to be relevant to extracts of atmospheric particles.

3. Persulfate can be a source of significant interference. However, its presence in ambient air particulate matter is considered unlikely.

4. Colloidal clay, as expected, is a strong interferent in the technique relying on light scattering for quantitation, viz., the $BaCl_2$ turbidimetric method. More surprising is its substantial interference in the MTS and AIHL microchemical methods with both positive and negative interference.

5. The only species showing a consistent trend in the direction (or sign) of the interference effect are as follows:

$SO_3^{=}$ (always positive)

$S_2O_8^{=}$ (always positive)

Ba^{+2} (always negative)

Barium is invariably a negative interferent since it reacts essentially irreversibly with sulfate. The possibility of a significant

barium extraction from glass fiber filters remains to be evaluated.

6. p-Benzoquinone is a significant interferent only for the MTB method which employs a wavelength of 460 nm for quantitation, at which yellow solutions absorb significantly. Since aqueous extracts from ambient air particulate samples will often be yellow, small positive errors by this method are possible unless results are corrected for sample blanks.

7. Phosphate exhibited, at most, a minor effect. In only one case, the modified Brosset method in acetone, was the interference effect negative and this result was only slightly beyond experimental uncertainty (i.e. beyond 1 σ). An acidic medium would be expected to minimize interference by barium phosphate precipitation. Nevertheless, comparing the three techniques employing acidic conditions (the AIHL microchemical, modified Brosset and turbidimetric methods with the MTB procedure which is run in basic solution, no significant differences were observed. The maximum interference was about 5%.

8. While cation exchange resins or complexing agents can effectively reduce or eliminate interference from cationic interferents elimination of effects of anionic interferents is more difficult.

9. It is difficult to assess the impact of these findings on the accuracy

of $SO_4^=$ analysis without knowledge of the concentration of these potential interferents in aqueous extracts from atmospheric particulate matter. For example calcium exhibits only a minor effect in the prèdent study, but it is found in relatively high concentration from water extraction of blank glass fiber filters and may also be extracted in significant amount from particulate matter. Thus its influence on the accuracy of sulfate determination may be substantial, especially with the AIHL micromethod.

V. PRECISION AND INTERMETHOD COMPARISON OF THE FOUR SULFATE PROCEDURES WITH ATMOSPHERIC SAMPLES (High Volume Samples)

A. Description of Experiment

To obtain samples sufficient to permit replication and analysis by the four methods, high volume samples were obtained from three sites, St. Louis, MO; Durham, NC; and Pasadena, CA. Four 24-hour filter samples were collected at each location plus two filter blanks which were used to adjust the data reported here.

To conduct an intermethod comparison with techniques differing widely in working range and for which the available sample was quite limited, a scheme was adopted to provide aliquots of appropriate concentration and volume for each method. One-inch discs were cut from each hi-vol filter, extracted in 5 ml of H_2O* and analysed by the AIHL microchemical method to establish the available sulfate in each sample. Based upon these results, the remainder of each filter was then extracted for 90 minutes in about 80 ml of boiling water under reflux and filtered. Each sample extract was diluted sufficiently to obtain a concentration of about 20 ug/ml sulfate except for filter blanks. These solutions were analysed directly by the MTR and turbidimetric methods. For the

*The extraction procedure consisted of immersion in water for two hours in a sealed test tube at 80°C.

modified Brosset and AIHL microchemical methods, further dilution into appropriate working ranges was necessary. All determinations were conducted with three replications except with the modified Brosset method. For the latter method, analysis was restricted to two replications because of insufficient solution.

B. Analytical Precision

Results of the measurements for all samples, corrected for blanks are shown in Tables 15A, 15B and 15C.

Data for the MTB procedure are presented as obtained by working curves fit with both a linear and a third order regression line. Each determination shown represents the mean of three replications (two replications with Brosset) ± one sigma. The variability of the intermethod mean value reflects the range of results by the four methods not the variability of the individual mean values. The latter, however, have been pooled for each method over the four samples from each location and the resulting pooled sigma values are used to estimate the precision of each method.

The precision of all methods as measured by coefficients of variation was 5% or better. Within this range, the most precise values at all locations were obtained with the modified Brosset and AIHL micromethods but these results were more variable with sampling location than was

Table 15b: Sulfate analysis of atmospheric hi-vol samples by four methods, St. Louis, MO ($\mu g/m^3$)[a]

Sample No.	EDTA titrn	Iodometric	Turbidimetric	Iodometric, KCl, linear regression	Iodometric, KCl, 3rd order regression	Incorporated[b] mean value (c.v., %)
0-397	33.7 ± .5	37.0 ± .2	36.3 ± 1.8	37.8 ± 1.0	38.5 ± .9	36.1 ± 1.9 (5.2)
0-398	34.4 ± .5	37.6 ± .9	37.3 ± 1.1	35.9 ± .8	40.4 ± .8	37.3 ± 2.2 (5.8)
0-397	25.0 ± .4	28.2 ± .3	27.7 ± .9	27.4 ± 1.1	28.3 ± 1.2	27.0 ± 1.5 (5.4)
0-397	23.1 ± .5	25.8 ± .5	25.1 ± 1.1	25.3 ± 1.2	25.2 ± 1.2	24.9 ± 1.1 (5.4)
Mean	29.1	32.2	31.6	32.6	33.4	
p value	0.5	0.3	1.3	1.0	1.0	
Coeff. of Var. (%)	1.6	1.0	4.2	3.2	3.1	

[a] Results are mean values ± 1 σ

[b] Mean excluding Iodometric result by 3rd order regression. The p value and coefficient of variation above reflect the range of results by the four methods, not the pooled variabilities of each mean.

Table 15b: Sulfur analysis of atmospheric hi-vol samples by four methods, Tacoma, WA ($\mu g/m^3$)[a]

Sample No.	XRF, filters	Brewer: sorbitol	Turbidimetric	Technicon AA2, linear regression	Technicon AA2 2nd order regression	Intermethod[b] mean value (C.V., %)
WE3069	11.6 ± .48	11.9 ± .1	11.8 ± .4	12.6 ± .3	13.0 ± .3	12.0 ± .4 (3.7)
WE3070	12.3 ± .2	12.5 ± .3	11.9 ± .5	13.5 ± .1	13.9 ± .1	12.6 ± .7 (5.6)
WE3071	11.2 ± .1	11.6 ± .1	11.1 ± .7	12.4 ± .3	12.8 ± .3	11.6 ± .6 (5.5)
WE3066	14.0 ± .7	14.4 ± .2	14.0 ± .8	14.1 ± .6	14.6 ± .6	14.1 ± .6 (4.0)
Mean	12.3	12.6	12.2	13.2	13.6	
σ pooled	0.36	0.24	1.62	0.39	0.40	
Coeff. of Var. (%)	2.9	2.0	5.2	3.0	2.9	

[a] Results are mean values ± 1 σ

[b] Same as in Table 15A

| | | |

experienced with the other methods. The turbidimetric method yielded the poorest precision except with the California samples.

It should be emphasized that in this study employing high volume samples, solutions were diluted to yield sulfate values in the optimal range of each method. In routine use with samples yielding a wide range of sulfate concentrations, somewhat poorer precision can be expected.

C. Equivalence of Methods

Considering next the degree of agreement between the methods, the range in values for all methods was approximately 10% of the intermethod mean for each sample. The coefficient of variation of the intermethod mean was surprisingly constant, ranging between 3.4 and 6.0%, considering the substantial variation in expected composition of the samples. While still yielding agreement within about 10%, the St. Louis samples led to the poorest agreement. In this case, the AIHL micromethod yielded consistently low values relative to the other techniques. One aqueous extract from St. Louis was subsequently shown to contain relatively high calcium concentrations (about 32 ug/ml) providing a likely explanation.

In comparing the methods of data reduction for the MTB method we note that all solutions analyzed were in the approximately linear portion of the working curve (i.e. 10-30 ug/ml) although the filter blanks were lower. Even in the "linear range", however, a third order line provides

a somewhat better fit to the S-shaped curve. The resulting concentrations (corrected for blanks) differ by up to 10% with third order results always higher. The difference diminishes with increasing concentration (in $\mu g/m^3$). Data by linear regression are invariably closer to results by the three other methods. We conclude that, within the approximately linear range, linear regression is the technique of choice.

D. Interference Effects

From each of the 12 high volume glass fiber filter samples, a 1" disc was extracted and analysed by the AIHL microchemical method. Three aliquot sizes were taken from the aqueous extract to insure samples in the optimal working range of the method, corresponding to absorbance values $0.3 \leq A \leq 0.7$.

In contrast to the samples from Durham and Pasadena the apparent $SO_4^=$ values from the St. Louis samples proved to be strongly dependent on aliquot size as shown by the example (HI3067):

Aliquot size, ml	Absorbance	$SO_4^=$ $\mu g/m^3$
0.10	0.612	28.6
0.20	0.718	16.9
0.40	0.660	7.5

Thus aliquot size dependence was observed even within the working range.

The influence of aliquot size suggested analytical interference as the

cause. Since calcium was suspected as a probable interferrent, the aqueous extracts from one St. Louis sample and one Pasadena sample were analyzed for calcium by flameless atomic absorption. Other interferents were possibly present but were not determined.

Sample Site (No.)	Ca^{+2} µg/ml	$SO_4^=$ µg/ml[AA]	$Ca^{+2}/SO_4^=$
St. Louis (23067)	32	111	0.29
Los Angeles (23063)	4	24.2	0.17

Based upon the observed ratio of $Ca^{+2}/SO_4^=$ and previous interference studies a negative error of about 15% in the sulfate value for the St. Louis sample would be expected when operating in the working range of the method.

The interference effects were further explored by subjecting portions of each extract to the cation exchange treatment (Reeves Angel, strong acid form) employed with the modified Brosset procedures. Table 16 lists selected results from this study comparing results with and without ion exchange treatment. The data compared for a given filter were obtained at approximately equivalent aliquot sizes.

The results suggest little effect of ion exchange on the California

[AA] By the AIHL micromethod on the extract obtained as described above. The value for St. Louis obtained with an 0.1 ml aliquot, is considered a minimum.

Table 16: THE INFLUENCE OF ION EXCHANGE TREATMENT ON HIGH VOLUME FILTER SAMPLES ANALYZED BY THE AIHL MICROCHEMICAL METHOD

Sample ID	$SO_4^{=}$ ($\mu g/m^3$)[a] With Ion Exchange	Without Ion Exchange	Ratio With/Without Ion Exchange
N #3056HV	10.7	9.62	1.11
N #3059HV	11.4	10.4	1.10
N #3071HV	12.9	9.95	1.30
N #3066HV	16.3	14.4	1.15
N #3067HV	06.5	05.0	1.05
N #3060HV	06.9	04.4	1.10
N #3075HV	09.4	09.7	0.99
N #3073HV	08.4	01.9	1.00
O #3063HV	7.90	7.90	0.99
O #3064HV	3.75	3.95	0.95
O #3076HV	0.55	0.57	0.99
O #3077HV	3.53	3.51	1.01

[a]Results shown are for a single trial in all cases.

samples. However, with samples from North Carolina and St. Louis, the results were generally higher after ion exchange supporting the significance of cationic interferents in these cases.

E. Accuracy of the Sulfate Methods by Standard Additions

The design of this study was complicated by the difference in working ranges for the four methods and the differing concentrations of sulfate available from the samples for a given degree of dilution. High-volume filter sample extracts, diluted to approximately 20 μg/ml sulfate, were the starting points for the standard addition studies. The concentrations of sulfate without standard additions were obtained from the preceding intermethod comparison. Table 17 summarizes the experimental protocol followed.

Per cent recoveries are listed in Table 18 for each sample extract at the two levels of sulfate addition. Similar results are also included for the blank glass fiber filters extracts. All experiments were run with two or three replications.

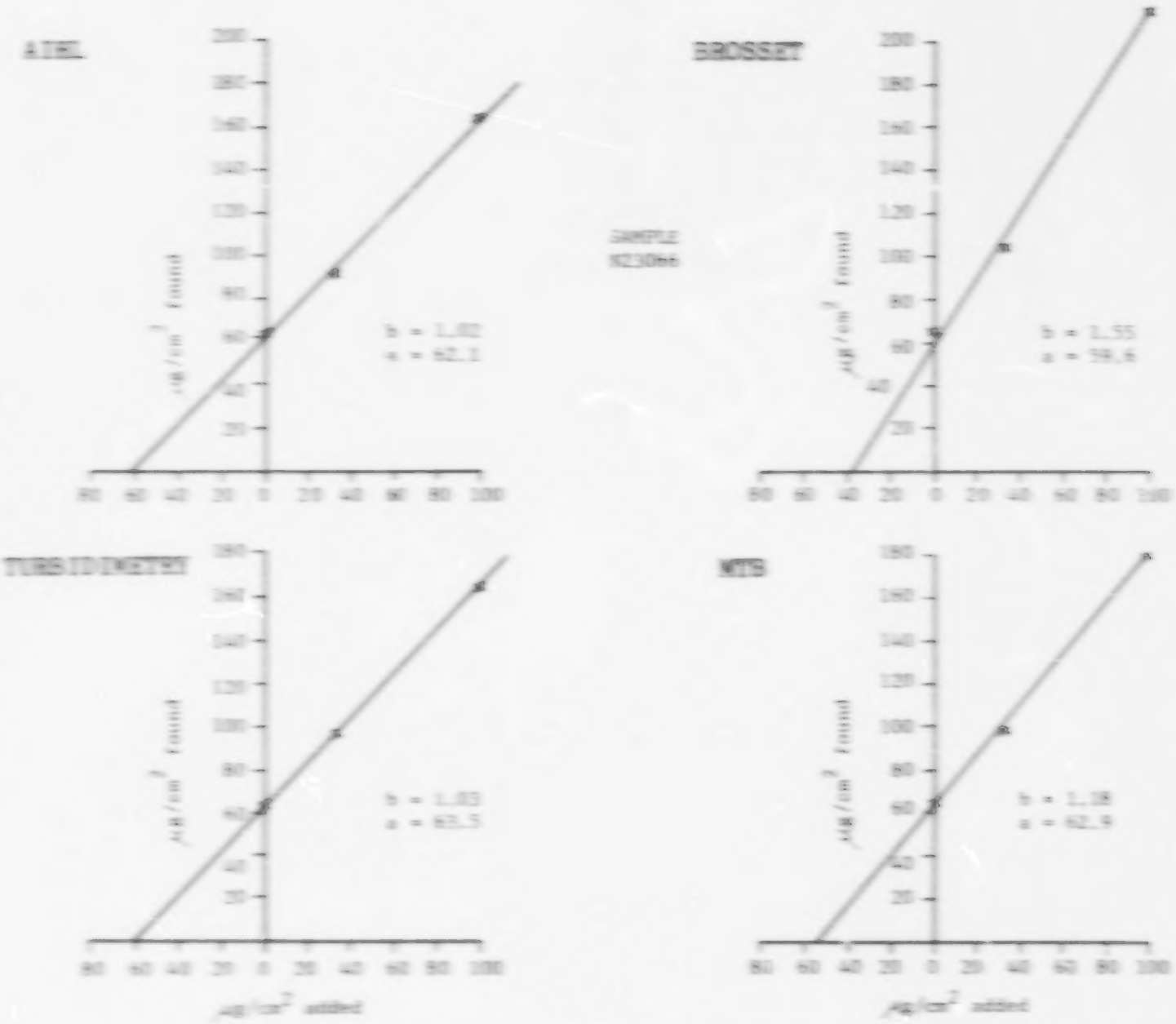
While these tables are useful for detailing the results, trends are difficult to discern from the inevitable experimental scatter. Interpretation is aided by plotting observed against added sulfate for each sample by each of the four methods. Such plots are presented in Figures 9-22. In place of concentration units in μg/ml, μg/cm^2 of filter

Table II. Method for Trace Amine Derivatization and Gas Phase Ultraviolet Spectroscopy

Amine	Volume of 1% ethanolic $AlCl_3$ added, μl	Volume 1 $\mu g/ml$ standard $HClO_4$ added, μl	Factor for further dilution prior to analysis	Final approximate concentration range analyzed, $\mu g/ml$
2(3)-Dimethylbut	1.00	10 and 30	5	5-20
Decylbut dimethyl	1.00	10 and 30	4 and 7	7
Tert-butylamine	10.0	100 and 500	none	30-50
Octylbutyl Ether	2.00	20 and 60	none	30-50

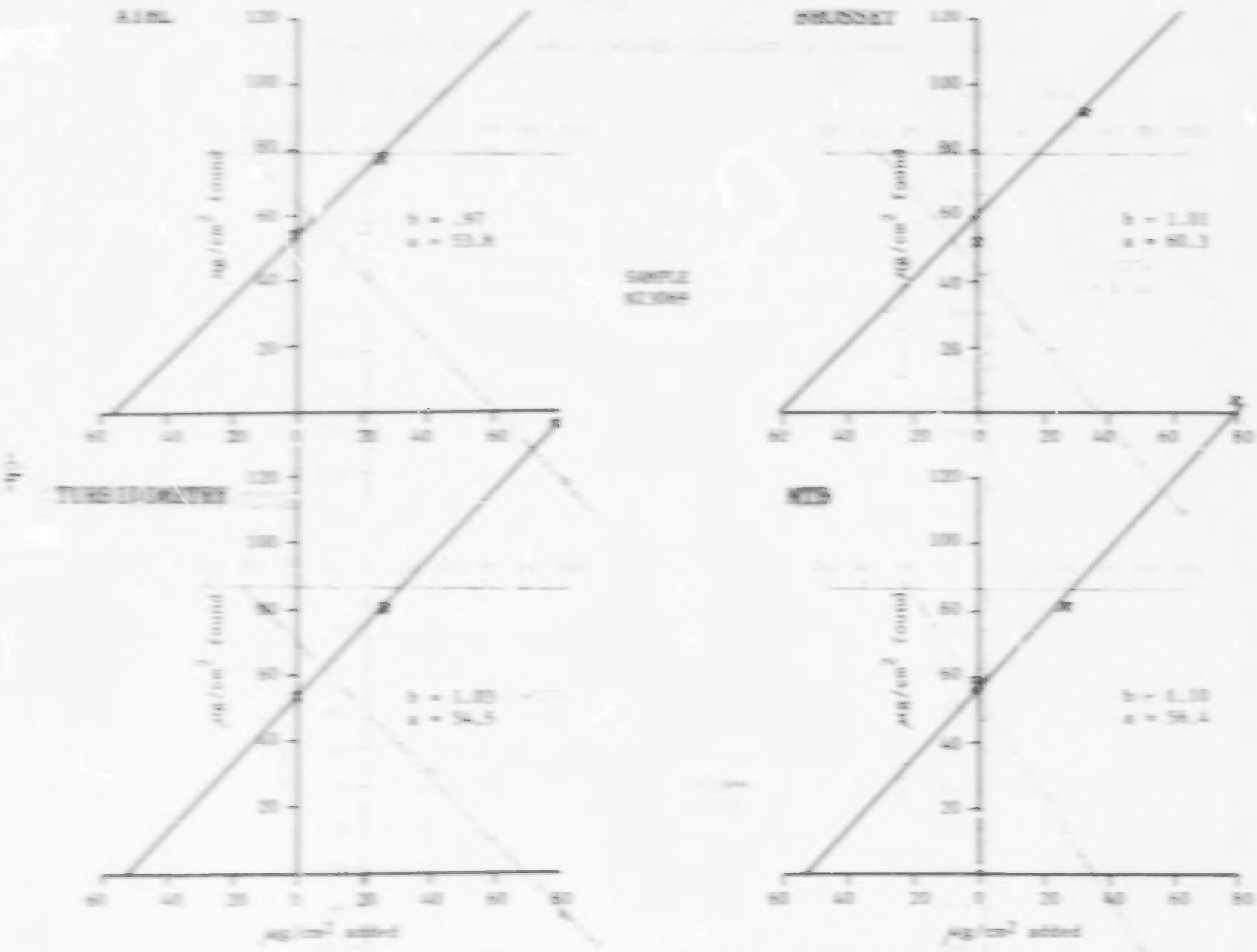
[a] All extracts were initially diluted to obtain about the same final concentration, 20 $\mu g/ml$ $HClO_4$.

[b] Solutions were diluted for analysis by the four procedures following the standard additions.



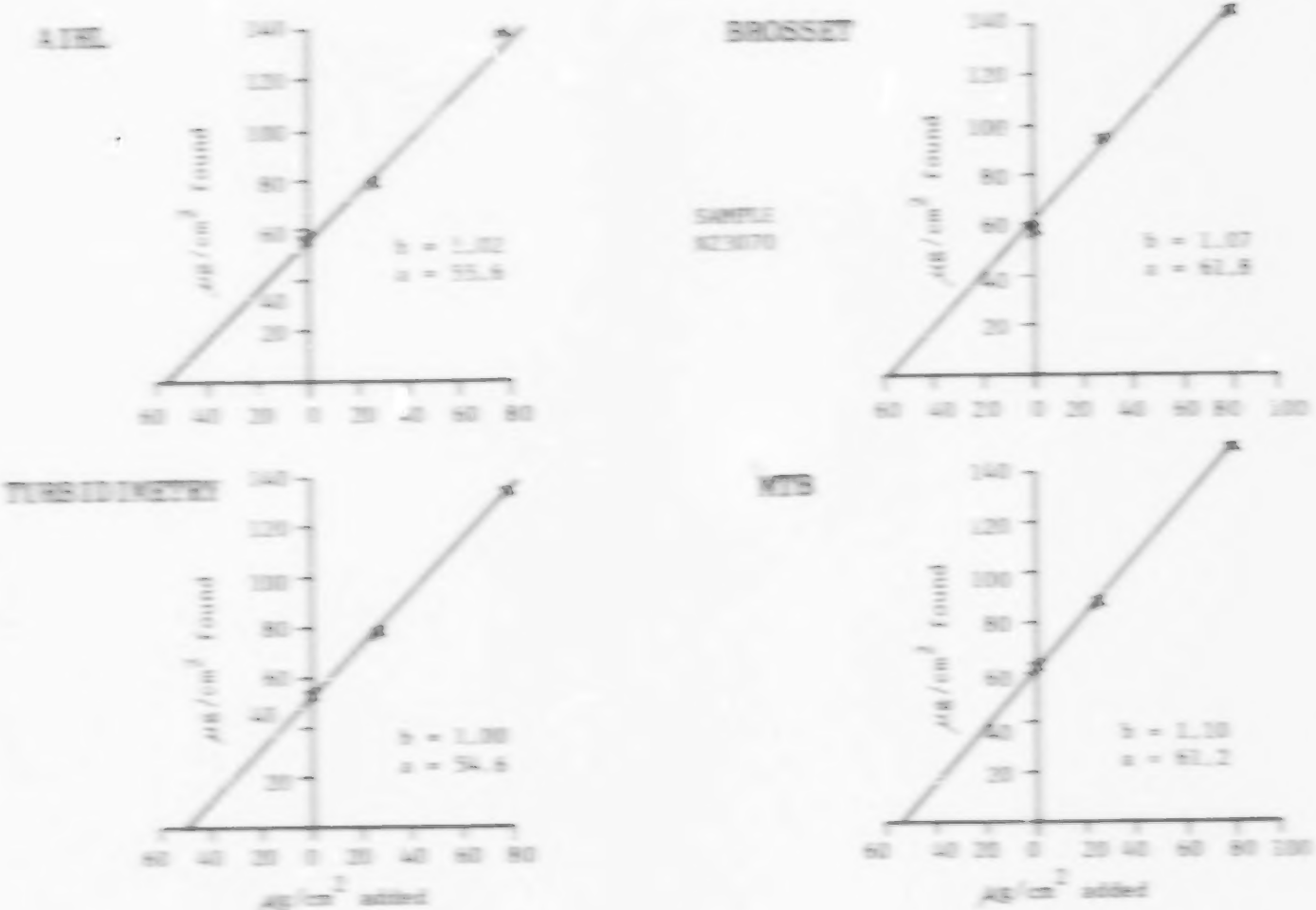
RECOVERY OF SULFATE FROM STANDARD ADDITIONS TO ATMOSPHERIC SAMPLES

Figure 9



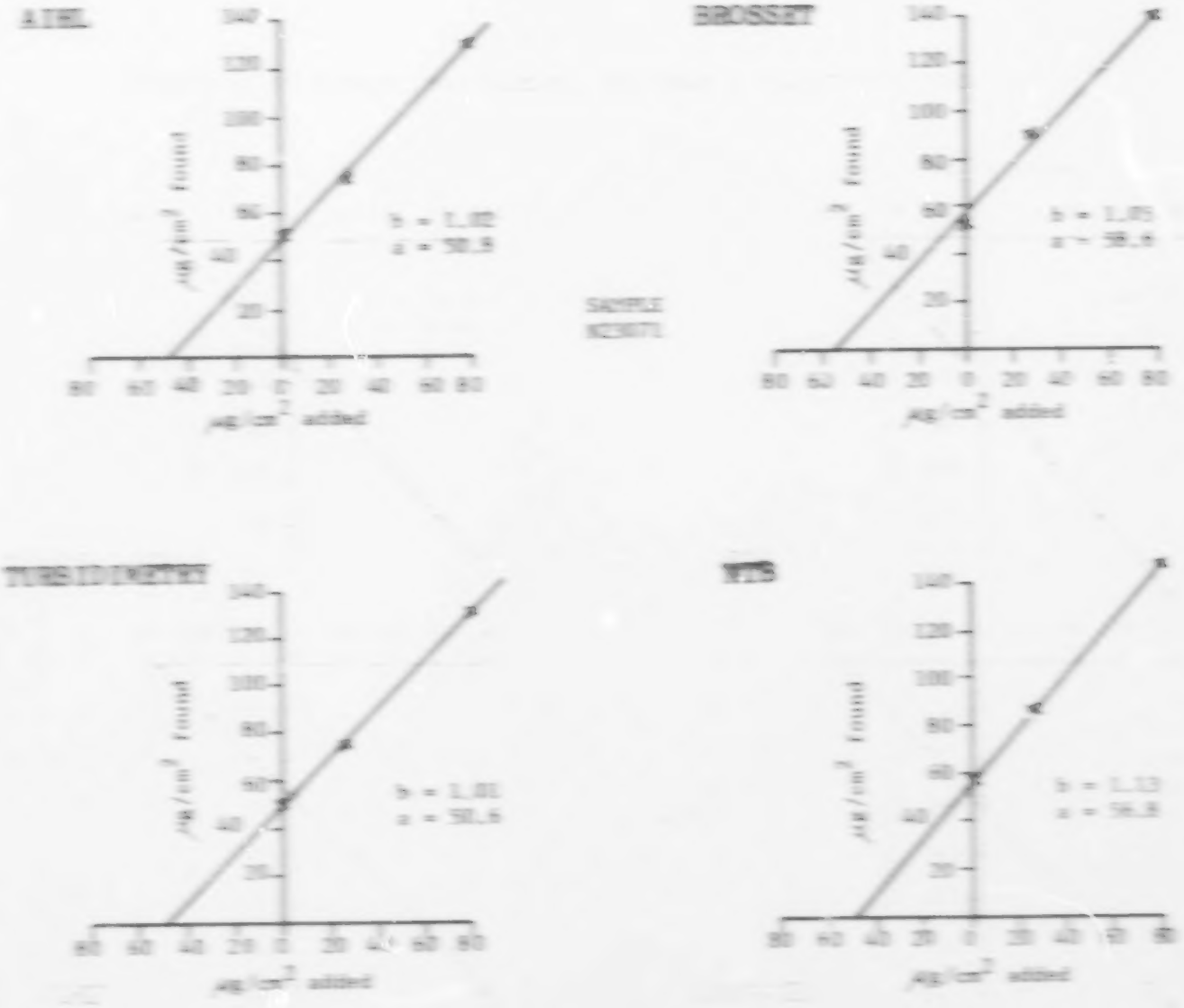
RECOVERY OF SULFATE FROM STANDARD ADDITIONS TO ATMOSPHERIC SAMPLES

Figure 10



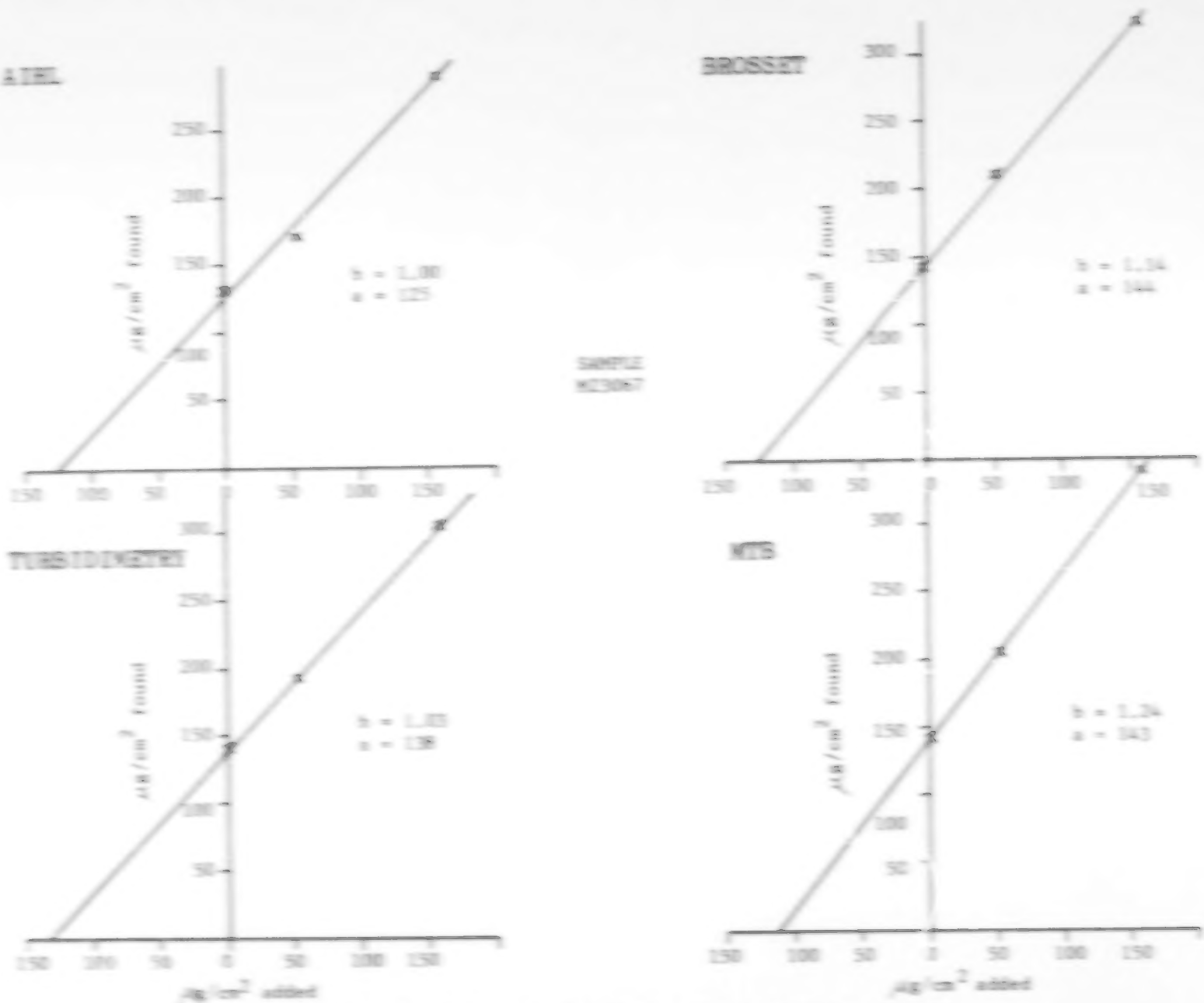
ALLOCATION OF SULFATE FROM STANDARD ADDITIONS TO ATMOSPHERIC SAMPLES

Figure 11.



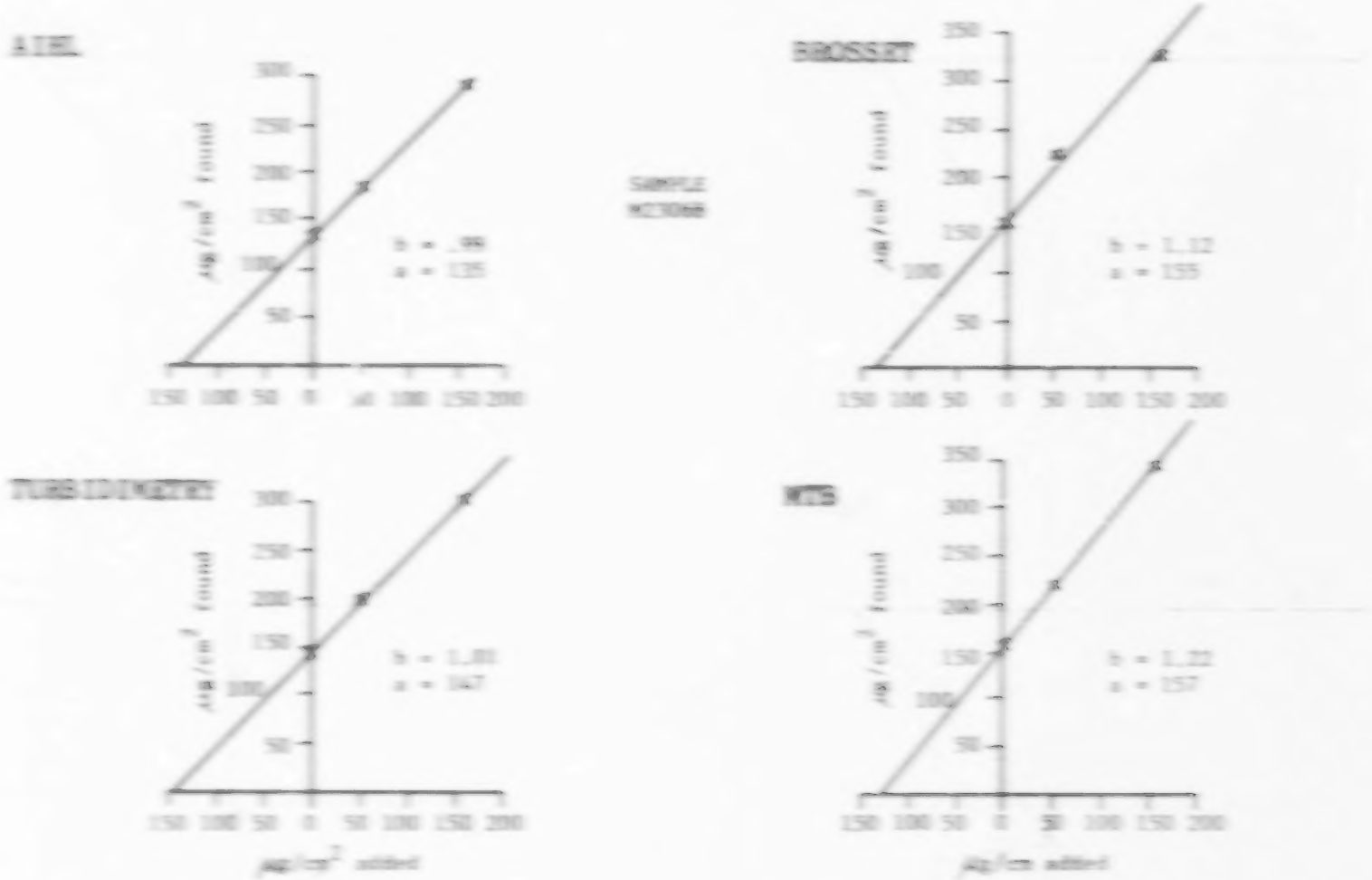
RECOVERY OF SULFATE FROM STANDARD ADDITIONS TO ATMOSPHERIC SAMPLES

Figure 12



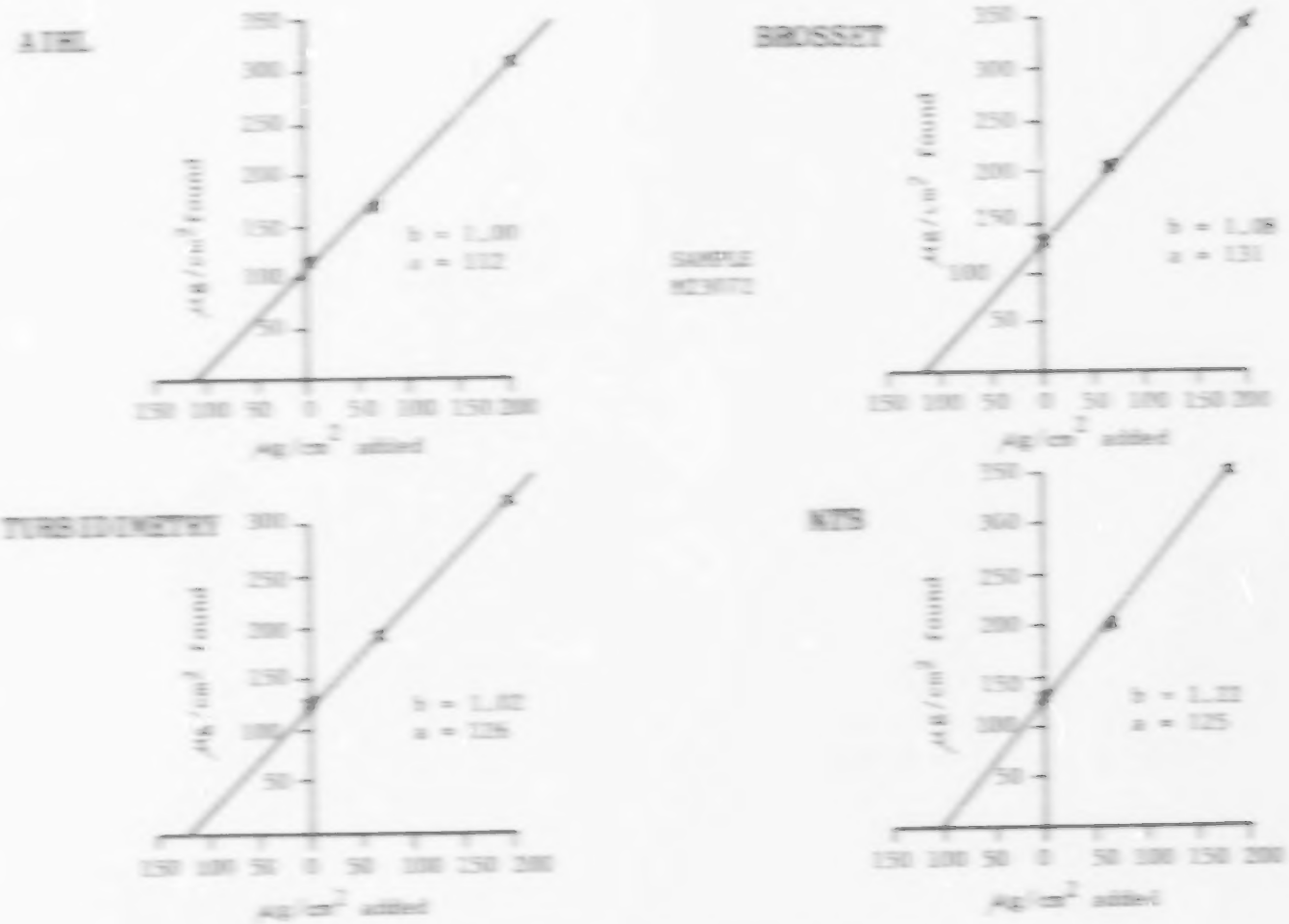
RECOVERY OF SULFATE FROM STANDARD ADDITIONS TO ATMOSPHERIC SAMPLES

Figure 23



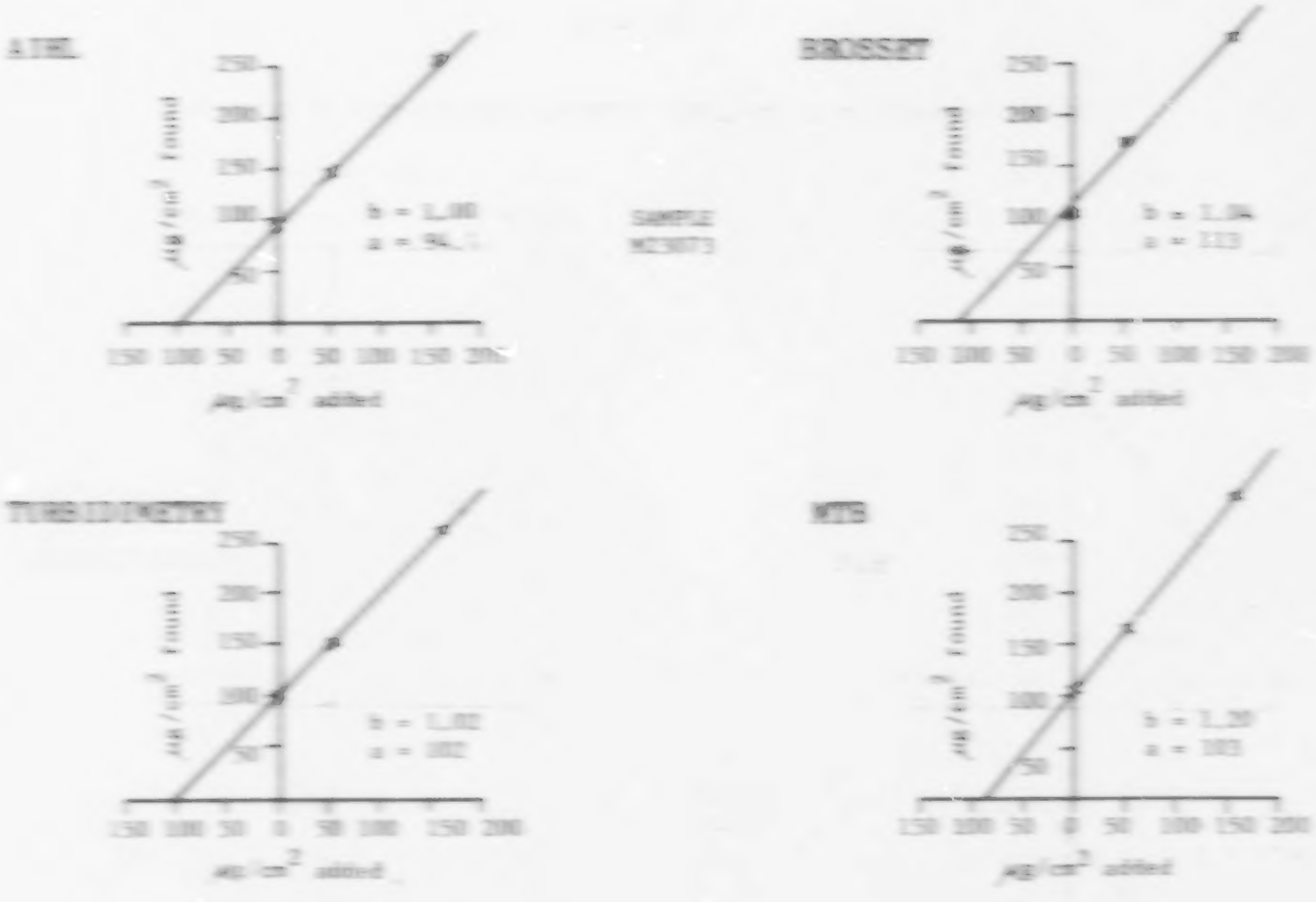
RECOVERY OF SULFATE FROM STANDARD ADDITIONS TO ATMOSPHERIC SAMPLES

Figure 1A



RECOVERY OF SILVER FROM STANDARD ADDITIONS OF ATMOSPHERIC SAMPLES

Figure 25



RECOVERY OF SILICATE FROM STANDARD ADDITIONS TO ATMOSPHERIC SAMPLES

Figure 15

BROSSET
GUTE
SAMORE
CHOCO
ALTE
DIE

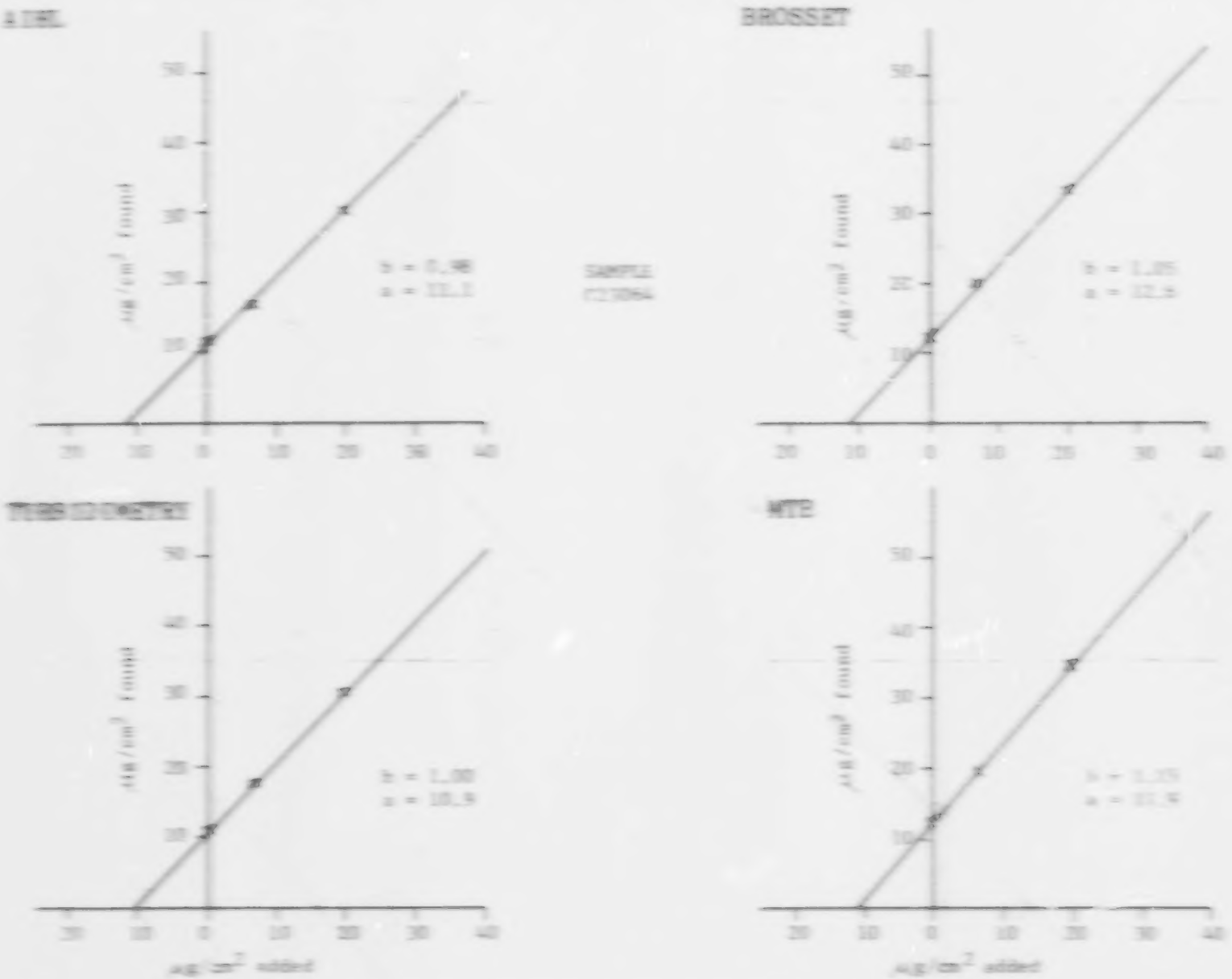
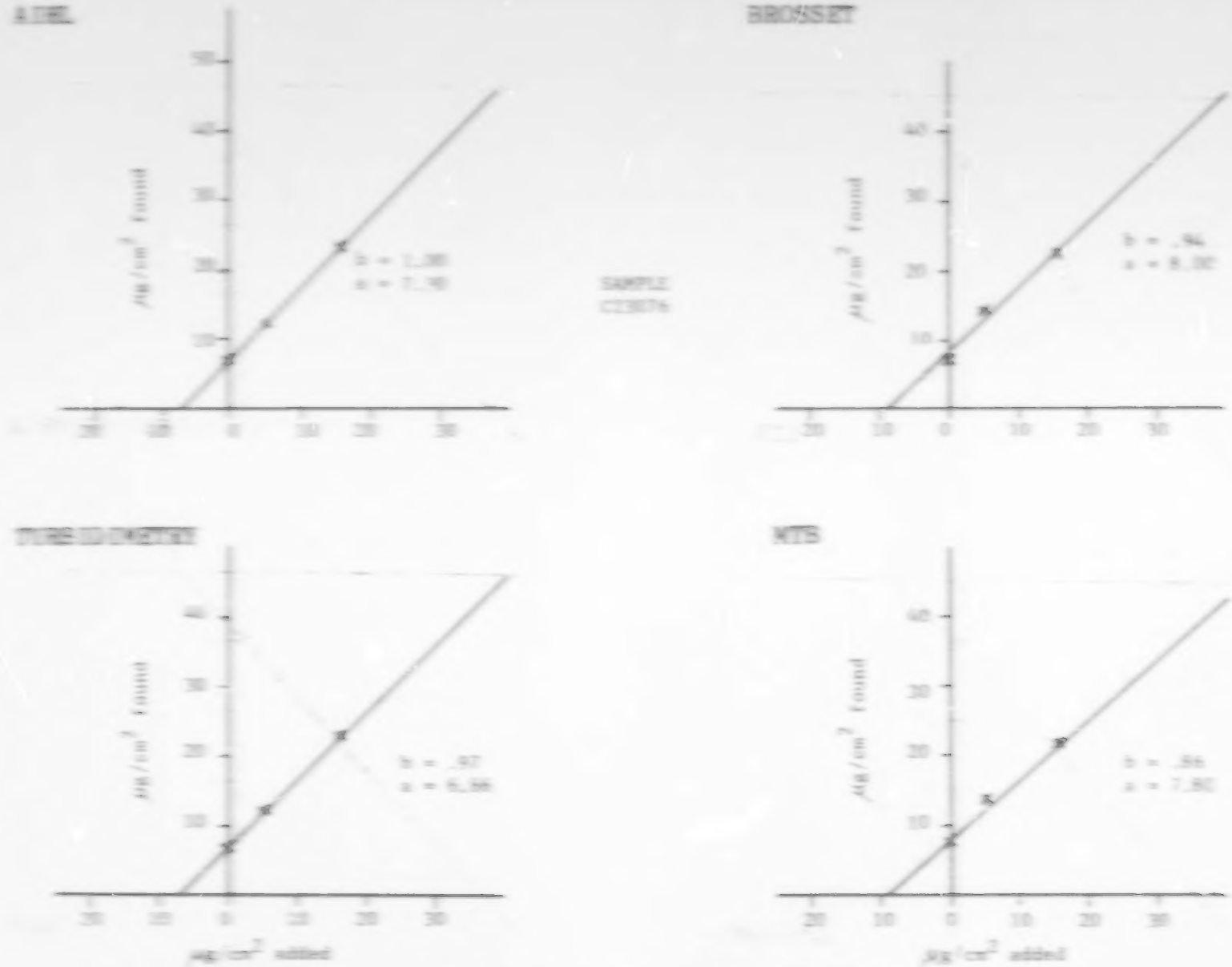


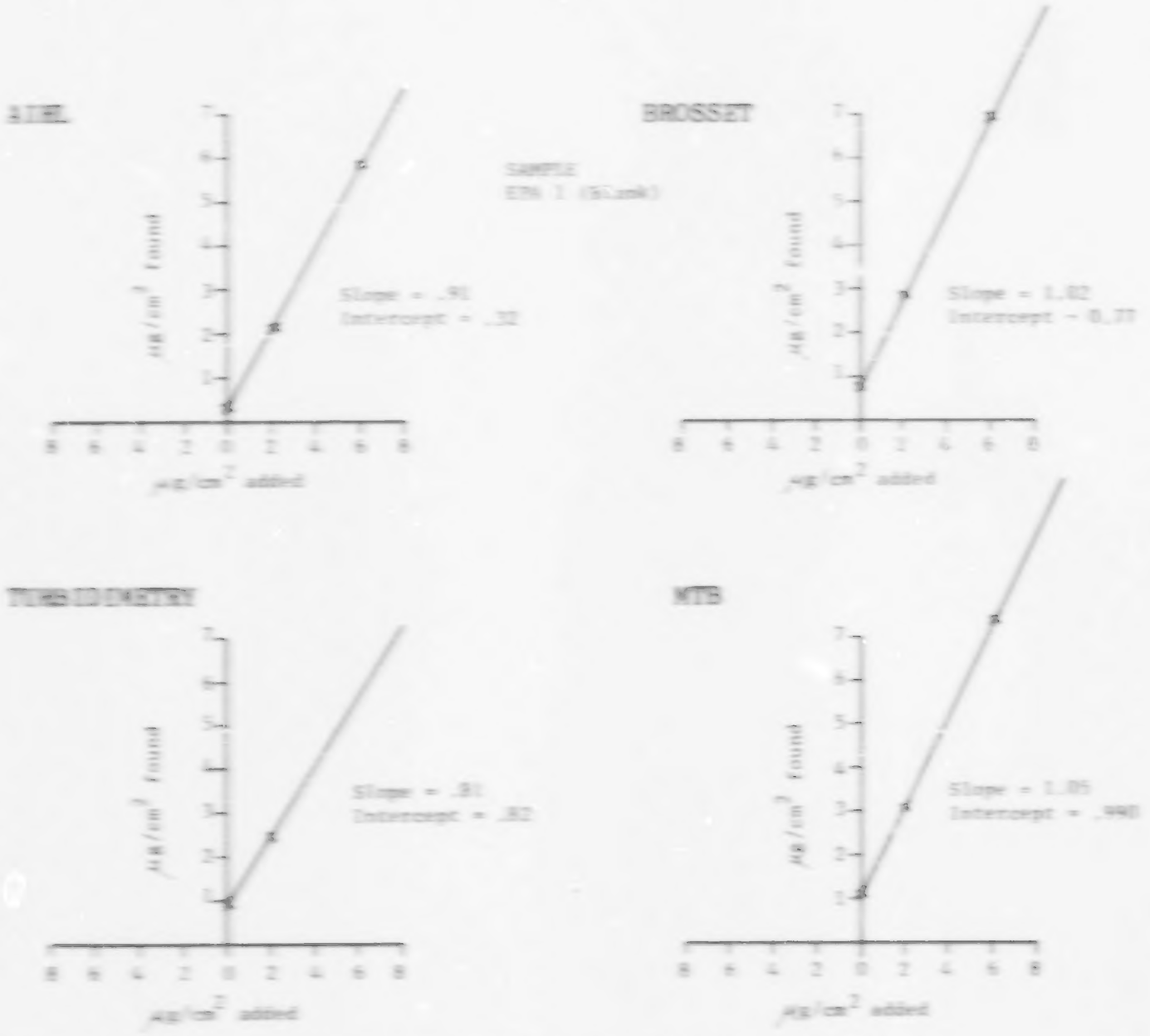
Figure 10

BRUSSET
KCB
ATEL
ENGELHARD
SAMPLE CONFIG



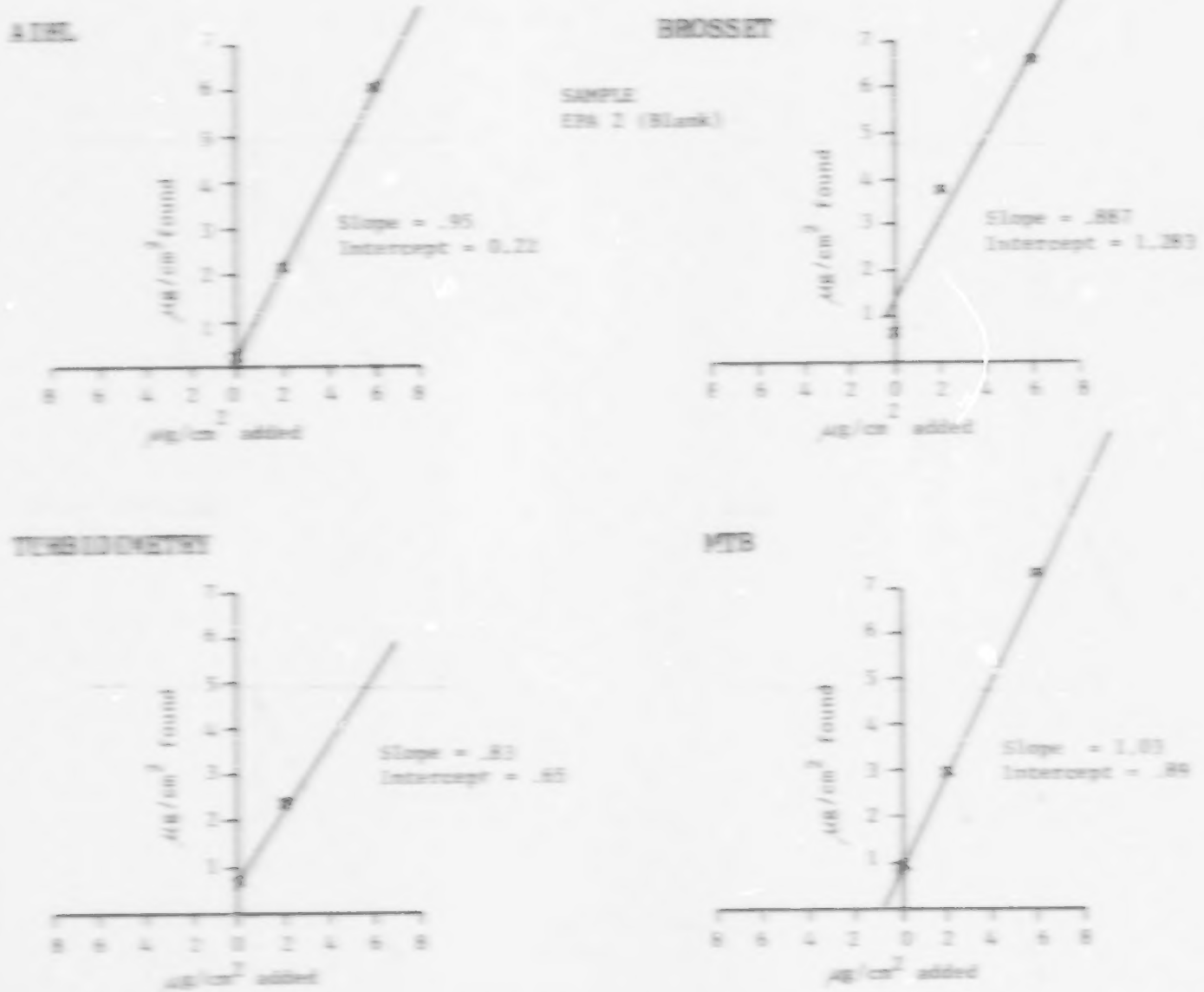
RECOVERY OF SULFATE FROM STANDARD ADDITIONS TO ATMOSPHERIC SAMPLES

Figure 20



RECOVERY OF SULFATE FROM STANDARD ADDITIONS TO ATMOSPHERIC SAMPLES

Figure 11



RECOVERY OF SULFATE FROM STANDARD ADDITIONS TO ATMOSPHERIC SAMPLES

Figure 22

are shown since this was an easier parameter to determine.

While these plots often appeared non-linear the number of data points was judged inadequate to attempt anything but linear regression. For such plots a least squares slope (b) of 1.00 represents a mean recovery of 100%. These plots may be examined for their mean recoveries, the degree of scatter about the least squares line, and non-linearity. Finally, Table 19 summarizes the least squares slopes and the results of an analysis of covariance to test for significant difference in slopes for the samples from a given site.

From these data and displays we make the following observations:

1. Comparing recoveries at the low and high levels of added sulfate, the Modified Brosset procedure, with only one exception, yielded lower recoveries at the higher level. The remaining techniques generally exhibited the opposite trend. Such observations would result in non-linear plots for sulfate found against sulfate added. The plot for sample NC2 0066 by the Brosser procedure was tested and found by analysis of variance to be significantly non-linear ($F(1,5) = 75$).

2. Mean recoveries by the AIHL microchemical and turbidimetric methods were close to 100% for all samples at all sites.

Table 19: MEAN FRACTIONAL RECOVERIES OF SULFATE WITH STANDARD ADDITIONS[a]

Pasadena, CA

Sample ID	AIHL Micro	Turbidimetric	Technicon, MTB	Modified Brosset, Acetone
C-23063	1.0	1.0	1.0[b]	1.0
64	1.0	1.0	1.1[b]	1.0
76	1.0	1.0	0.9[b]	0.9
77	1.0	1.0	1.1[b]	1.0

St. Louis, MO

M-23067	1.0	1.0	1.2	1.1
68	1.0	1.0	1.2	1.1
72	1.0	1.0	1.0	1.1
73	1.0	1.0	1.0	1.0

Durham, NC

N-23069	1.0	1.0	1.1	1.0[b]
70	1.0	1.0	1.1	1.1[b]
71	1.0	1.0	1.1	1.0[b]
66	1.0	1.0	1.0	1.0[b]

[a] As measured by the least squares slope of plots of sulfate found against added sulfate.

[b] Recoveries within the set of four samples are significantly different at 99% level by analysis of covariance.

3. Recoveries by the MTB method were 10-20% high in 63% of the experiments, 5-10% high in 25% of the experiments and -5 to 5% high in the remaining. Considering mean recoveries for each sample, recoveries were, with one exception, high by 10-20%.

4. Recoveries by the modified Brosset method were 10-50% high in 66% of all experiments with remaining results between -2 and 10% high. Mean recoveries by this method ranged from 90 to 110%. Mean recoveries were close to 100% with Pasadena samples and generally above 100% with St. Louis and Durham samples.

5. Recoveries from spiked blank filter extracts are somewhat lower than those from the particulate samples. Comparing the two procedures with ion exchange pretreatments (MTB and modified Brosset) to the two lacking such treatment, recoveries with the blanks are systematically higher with pretreatment. These findings suggest the importance of cationic interferents, such as calcium, extracted from glass fiber filters. Failure to observe similar trends with the atmospheric samples is not surprising considering the possibility of positive interferents extracted from the samples.

6. Comparing the present results to the intermethod comparison reported in Table 15 the Technicon MTB has, in both cases yielded somewhat higher sulfate values. Furthermore these results are consistent with preliminary findings summarized in II A and Figure 1.

F. Summary and Conclusions

Employing high volume filter samples the four wet chemical methods yield agreement within about 10% for all samples. Within this range the poorest agreement was found with St. Louis samples; this appears to be relatable to the influence of cationic interference. The degree of equivalence found, in spite of the varying sensitivity of the methods to interferents, suggests that with such large samples, interference effects are minimal. The coefficient of variation of the four methods was 5% or less.

While agreeing within about 10% the modified Brosset and WTB methods gave consistently higher values in analysis of the high volume filter samples compared to the remaining procedures. Standard addition results also demonstrated more than 100% apparent sulfate recoveries by these methods in > 80% of all experiments implying that a systematic positive bias is the cause of the higher results by the methods with the atmospheric samples.

The degree of agreement found suggest that the choice of a method from among these four, for analysis of high volume samples can be based upon such factors as cost per determination or experimental convenience. The restricted range of both the modified Brosset and AIHL micromethod clearly makes them inappropriate for consideration with high volume samples.

VI. EQUIVALENCY OF WET CHEMICAL AND X-RAY FLUORESCENCE METHODS AND INFLUENCE OF SAMPLING DESIGN WITH ATMOSPHERIC LOW VOLUME FILTER SAMPLES

A. Description of the Experiment

Details of the sampling design were discussed in the introduction. This design permits surface analysis method comparisons employing both glass fiber and Fluoropore filters each with two particle size fractions (i.e. 0-20 μm and 0-2 μm). Furthermore, since all sampling was conducted simultaneously, results obtained on glass fiber and Fluoropore may be compared as well as the influence of sampler (i.e. High volume vs. low volume).

Fluoropore filters mounted in plastic frames were initially analyzed by XRFA at Research Triangle Park. Following shipment to Berkeley, 1" (25 mm) discs were removed from the center of each filter and the samples hand-carried for XRFA at the Lawrence Berkeley Laboratory. Many of the 1" discs curled up badly after their removal. Since the LBL technique requires constant distance between sample and detector it was necessary for the analyst to press the samples flat between glassine paper. Therefore, the loss of some S in handling is likely. Such loss would, of course, influence the subsequent wet chemical analyses as well. Following XRFA, the discs were returned to ARB.

Since the 37 mm Fluoropore filters had been glued into their plastic

frames it was not possible to include the remaining portion of the filters in the wet chemical determinations. The 1" discs were extracted by the micropercolation technique into 10 ml H_2O. The 37 mm glass fiber filters were received unmounted and the complete discs were extracted by the micropercolation technique into 10 ml H_2O. The resulting solutions provided sufficient sample for a single replication by each of three methods: the AIHL microchemical, MTR and modified Droseet methods. Accordingly, results are quoted without a statement of precision. However, the precision of the methods as established with the high volume filter extracts (i.e. C.V. $\leq$ 5%) represents a reasonable upper limit to the precision to be expected with low volume samples.

B. Results

1. Comparison of Wet Chemical Sulfate Analysis

Tables 20 and 21 detail results for Fluoropore and glass fiber filters, respectively, with filters identified by number and sampling date. For ease in interpretation of results, the data in Tables 20 and 21 have been pooled and recalculated relative to results with the MTR method as shown in Tables 22 and 23. The ratio of means are shown by sampling site for the four total particulate (0-20 μm) and refined particulate (0-3 μm) samples. Considering first the pooled Fluoropore results (Table 22) the MTR values are consistently higher than those by the AIHL microchemical

Table 21: SUMMARY OF LOW VOLUME GLASS FIBER FILTER SULFATE DETERMINATIONS ($\mu g/m^3$ sulfate)

Sample ID	Date Sampled	Brosset	Technicon	AIHL Micro
NC-1A[a]	7-15-74	14.1	16.8	15.0
NC-1B	7-15-74	9.48	11.8	11.4
NC-2A	7-16-74	15.4	18.6	15.1
NC-2B	7-16-74	14.5	18.8	14.5
NC-3A	7-17-74	12.2	16.6	14.9
NC-3B	7-17-74	10.9	15.6	14.3
NC-4A	7-18-74	15.2	19.3	18.0
NC-4B	7-18-74	14.5	19.1	17.9
MO-1A[a]	8-5-74	30.5	40.3	34.6
MO-1B	8-5-74	10.7	11.1	8.98
MO-2A	8-6-74	32.6	46.3	35.0
MO-2B	8-6-74	15.0	17.3	16.9
MO-3A	8-7-74	29.5	35.8	32.5
MO-3B	8-7-74	28.7	37.4	26.2
MO-4A	8-8-74	27.1	35.0	32.6
MO-4B	8-8-74	27.6	30.4	29.3
CA-4CTG[b]	12-2-74	6.72	6.86	6.64
CA-4DRG	12-2-74	6.90	7.60	6.79
CA-6CTG	12-7-74	4.29	3.97	3.87
CA-6CRG	12-7-74	2.97	3.40	2.78
CA-7CTG	12-6-74	7.25	1.74	1.36
CA-7DRG	12-6-74	1.90	1.64	1.52
CA-8CTG	12-9-74	3.86	2.76	2.25
CA-8DRG	12-9-74	2.40	1.42	1.12

[a]For North Carolina and Missouri samples A are total (0-80 μm) and B are refined (0-2 μm) particle samples.

[b]For California samples CTG indicates total and DRG, refined samples.

Table 32: RELATIVE RESULTS--FLUOROPORE FILTERS[a]

		WSB	Modified Brosset	AIHL	XRFA (EPA)	XRFA (IML)
Durham	Total	1.00	.78 ± .10	.93 ± .04	1.49 ± .08	.80 ± .04
	Refined	1.00	.84 ± .09	.91 ± .02	1.38 ± .01	.79 ± .01
St. Louis	Total	1.00	.89 ± .05	.81 ± .00	1.30 ± .04	.77 ± .03
	Refined	1.00	1.15 ± .16	.88 ± .01	.93 ± .06	.58 ± .04
Pasadena	Total	1.00	1.28 ± .13	.70 ± .08	1.07 ± .10	.54 ± .06
	Refined	1.00	1.11 ± .13	.64 ± .04	.89 ± .04	.60 ± .09

[a]Results are expressed as the ratio of the means of determinations on four samples. Errors are calculated as the standard deviation of the ratio of two dependent variables:

$$\sigma_{\left(\frac{\bar{x}}{\bar{y}}\right)} = \sqrt{\text{var.}\left(\frac{\bar{x}}{\bar{y}}\right)} \quad \text{and var.} \frac{\bar{x}}{\bar{y}} = \left(\frac{\bar{x}}{\bar{y}}\right)^2 \left[\frac{\sigma_{\bar{x}}^2}{\bar{x}^2} + \frac{\sigma_{\bar{y}}^2}{\bar{y}^2} - 2\,\frac{\text{cov}(\bar{x},\bar{y})}{\bar{x}\cdot\bar{y}} \right]$$

This technique, we believe, eliminates the variability in the ratio due merely to day to day changes in the sulfate concentrations for the four samples pooled.

Table 23: RELATIVE RESULTS--GLASS FIBER FILTERS (Low Vol)[a]

		HTB	Modified Brosset	AIHL
Durham	Total	1.00	.80 ± .02	.88 ± .03
	Refined	1.00	.76 ± .02	.89 ± .05
St. Louis	Total	1.00	.76 ± .03	.85 ± .04
	Refined	1.00	.88 ± .03	.94 ± .02
Pasadena	Total	1.00	1.40 ± .45	.87 ± .02
	Refined	1.00	1.10 ± .05	.85 ± .03

[a]Same as footnote a, Table 22.

methods while the modified Brosset results were more variable and highly site dependent.

Table 23 shows a similar comparison but using samples collected on glass fiber filters. The MTB method yields results generally higher than those by the modified Brosset and the AIHL microchemical method while the latter two methods agreed well except for California samples.

2. X-ray Fluorescence Results

A comparison of XRFA results obtained at Research Triangle Park and the Lawrence Berkeley Laboratory is shown in Table 24. While results by the two laboratories are clearly highly correlated, they differ by nearly a factor of two with LBL results lower. The difficulties experienced at LBL because of the poor quality of the samples are improbable sources of so constant a discrepancy in results.

Previous comparisons of LBL-XRFA sulfur with wet chemical sulfate analyses used the AIHL micromethod with Gelman GA-1 cellulose acetate membrane filters. The samples studied had been collected at various locations in California's South Coast Basin. The mean ratio wet chemical $SO_4^=$/XRFA S as $SO_4^=$ was 1.01 ± .06 for 400 filters.[3]

In the present study the degree of agreement between XRFA and wet chemical sulfate is significantly affected by choice of wet chemical

Table 24: COMPARISON OF EPA AND LBL X-RAY FLUORESCENCE RESULTS ON LOW VOLUME FLUOROFORE FILTERS

Sample ID		R(LBL)/R(EPA)
BC-1C		0.53
BC-1D		0.66
BC-2C		0.57
BC-2D		0.54
BC-3C		0.55
BC-3D		0.50
BC-4C		0.52
BC-4D		0.50
MO-1C		0.58
MO-1D		0.60
MO-2C		0.55
MO-2D		0.68
MO-3C		0.67
MO-3D		0.64
MO-4C		0.60
MO-4D		0.58
CA-4ATF		0.58
CA-4BRF		0.71
CA-6ATF		0.55
CA-6BRF		0.70
CA-7ATF		0.46
CA-7BRF		0.52
CA-8ATF		0.44
CA-8BRF		0.66
	Overall	0.56

method. When LBL-XRFA and the AIHL micromethod are compared, the ratio of means $SO_4^=$/XRFA S as SO_4 = 1.18. If MTR results are used the ratio becomes even higher. Since XRFA results should be greater than or equal to wet chemical findings (i.e. the ratio should be $\geq$ 1.0) we conclude, based upon the present findings as well as prior experience, that the current LBL results are too low.

Considering the comparison of RTP-XRFA and wet chemical analyses, again the degree of agreement depends markedly on the choice of wet chemical method. When compared against the MTR procedure as in Table 21 Pasadena results are within about 10% of those obtained wet chemically. At Durham, results are significantly higher by XRFA with mixed findings at St. Louis.

Considering the influence of particle size on the XRFA results, as shown in Table 21, in all cases the RTP-XRFA results, relative to MTR, were higher with total particulate than with refined particulate samples. On average the ratio of total/refined XRFA sulfur was 1.23 which is suspiciously close to the ratios of correction factors used in correcting the RTP-XRFA for self absorption. For total filters 19% self absorption was assumed by T. Dzubay compared to 15% for refined samples, yielding a ratio of corrections of 1.27. Thus the apparent differences in agreement between RTP-XRFA and MTR for total and refined samples may not be real.

3. The size distribution of sulfate

While not a direct objective of this study the proportion of refined (0-2 μm) to total (0-20 μm) particulate sulfate may be seen in the data listed in Tables 20 and 21. Results have been pooled by sampling site for the Fluoropore filters as shown in Table 25. The striking observation here is the importance of large particle sulfate with St. Louis samples.[AA]

4. Comparison of sulfate results on glass fiber and Teflon filters

The present study provides one of the few data sets in which sulfate results on glass fiber filter samples may be compared to those on a relatively inert filter of equivalent filtration efficiency.[A]

Results for corresponding glass fiber and Fluoropore filters are compared in Table 26 as the ratio of means. Glass fiber sulfate values with total filters are systematically higher at Durham and St. Louis but approximately equivalent at Pasadena. With refined

[A]The filtration efficiency of Fluoropore filters (FALP, 1 mu pore size) was recently studied by Prof. Benjamin Liu, University of Minnesota. Results were provided by private communication from Prof. Liu, 1975.

[AA]It is believed by the EPA staff that much of this large particle sulfate resulted from a nearby industrial source of $CaSO_4$.

| | | |

Table 05: THE MEAN FRACTION OF SULFATE IN REFINED (0-2 μm) PARTICLES [a].

Durham	1.07
St. Louis	0.69
Pasadena	0.36

[a] Results obtained by pooling Fluorocore results for analysis by the MRD, AIHL microchemical and modified Brosset methods.

samples results at Durham and St. Louis are much closer to being equivalent on the two filter types.

If oxidation-promoting species (e.g. Fe, Ni, Mn, Cu) were largely restricted to particles sizes > 2 μm then the present data would permit additional mechanistic interpretation. Table 27 lists the XRFA results from T. Dzubay, EPA, for the metals mentioned above. While some results are below limits of detection, results do, indeed indicate a predominance of these elements in the total filters (0-20 μm) compared to the refined (0-2 μm) particle samples. Thus the present data are consistent with enhanced artifact sulfate formation on glass fiber filters in the presence of oxidation-promoting species.

5. <u>The influence of sample size on sulfate results with glass fiber filters</u>

Sulfate results on low and high volume glass fiber filters are compared in Table 28. The trends are very similar to those for glass fiber/Fluoropore ratios; Durham and St. Louis results are consistently higher on the low volume samples. Total air volumes sampled was 3 m^3/cm^2 for the high volume sampler compared to 2 m^3/cm^2 for the low volume units. Thus the present results are consistent with previous studies of the "sulfate anomaly"[4,5] which demonstrated that apparent sulfate levels increased with decreasing air volume sampled.

| | | |

Table 36: COMPARISON OF LOW (0-20 μm) AND HIGH VOLUME GLASS FIBER FILTER SULFATE RESULTS[a]

Sampling Site/Date	MTD	Low Volume/High Volume Dressel	AIHL
HC 7-15-74	1.33	1.16	1.07
HC 7-16-74	1.38	1.02	1.03
HC 7-17-74	1.34	1.05	1.33
HC 7-18-74	1.37	1.06	1.09
HC Overall	1.36 ± 0.01	1.12 ± 0.04	1.20 ± 0.02
MC 8-5-74	1.07	.80	1.03
MC 8-6-74	1.17	.87	1.00
MC 8-7-74	1.31	1.05	1.28
MC 8-8-74	1.30	1.05	1.41
MC Overall	1.21 ± 0.07	0.93 ± 0.06	1.16 ± 0.09
OA 12-2-74	1.02	.90	0.89
OA 12-7-74	.96	1.15	0.80
OA 12-8-74	.76	1.34	0.59
OA 12-9-74	.82	1.23	0.71
OA Overall	.93 ± 0.06	1.39 ± 0.38	0.79 ± 0.06
Overall (for 3 sites)	1.23 ± 0.05	1.00 ± 0.06	1.16 ± 0.06

Mean ratio low vol/high vol = 1.13 ± 0.04
(for 3 methods and 3 sites)

[a]Same as footnote a, Table 26

6. Comparison of high volume glass fiber and low volume Fluoropore filter sulfate results

The findings in Tables 26 and 27 suggest that the high volume and Fluoropore data should agree well. These results are compared in Table 29. The striking result here is the equivalence obtained with these filters at the three sites as measured by the HTB method in contrast to the more scattered results with the remaining methods. The modified Brosset and AIHL micromethods indicate opposite trends with location; the Pasadena site yielded the highest ratio with the modified Brosset procedure and the lowest, with the AIHL method. These trends are largely dictated by the relative results obtained on Fluoropore filters by the three methods as summarized in Table 22.

C. Summary and Conclusions

Results with low volume filters have revealed differences between the three wet chemical methods able to analyze these samples of up to a factor of 2 for individual samples and 1.6 when pooled by sampling site. This contrasts markedly with results obtained with high volume samples.

XRFA results by LBL and RTP differ by nearly a factor of two. The RTP XRFA permit estimation of water soluble sulfate within 10-50% of that obtained by the HTB method depending on location. Since Fluoropore and high volume results by the HTB method agree well, XRFA on Fluoropore and

Table 89: [illegible]

	[illegible]	[illegible]	[illegible]
Durham	1.04 ± .10	.05 ± .05	1.04 ± .06
St. Louis	.97 ± .06	[illegible]	.88 ± .08
Pasadena	1.04 ± .03	1.14 ± .11	.74 ± .07

[a]Same as footnote a, Table [illegible]

MTB analyses of high volume glass fiber filters, such as employed with the NASN network, are expected to agree within 10-50%, as well, for these sites.

Large particle (2-20 μm) sulfate was clearly observed in the St. Louis samples; about 90% of the total sulfate observed was in this size range. Such large particle sulfate was not observed in the Pasadena and Durham samples. In fact at Durham, the "refined" samples often yielded higher sulfate and sulfur than total filter samples suggesting possible sampling error.

The present data are consistent with artifact sulfate formation from SO_2 on the low volume glass fiber filter samples with enhanced $SO_4^=$ formation in the presence of a large particle-related oxidation catalyst(s) in the aerosol sampled. The equivalence of low volume Fluoropor total filter and high volume glass fiber sulfate results as measured by the MTB method implies an insignificant percentage of the sulfate results from sampling artifacts with 24-hour high volume glass filters.

Finally, in comparing the three wet chemical methods the modified Brosset procedure has, at times, yielded what we consider to be erratic behavior with the low volume samples. Of the remaining two only the MTB method provides protection against cationic interferents. Thus, in spite of the 10-20% positive error in the method revealed by studies with high volume samples, the MTB method is considered the most reliable of the

three for long term (e.g. 24-hour) low volume samples. For short term, low volume samples requiring a micro sulfate method we favor the AIHL microchemical method.

VII. REFERENCES

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4. Lee RE and Wagman J, Amer. Ind. Hygiene Assoc. J. 27 266 (1966)

5. DuRoto L, Zdrojewski A, Teichman T and Monkman H., Int. J. Environ. Anal. Chem 1 113 (1971).

Appendix A

(From Selected Methods for the Measurement of Air Pollutants Public Health Service Publication No. 999-AP-11 with modifications by AIHL)

Determination of Sulfate in Atmospheric Suspended Particulates: Turbidimetric Barium Sulfate Method[a]

INTRODUCTION

Suspended particulate matter is collected over a 24-hour period on an 8- by 10-inch glass fiber filter by using a high-volume sampler.[1] A water extract of the sample is treated with barium chloride to form barium sulfate. The turbidity caused by the barium sulfate is a measure of the sulfate content. Aliquoting is adjusted so that samples containing 1 to 20 $\mu g/m^3$ (the expected range of atmospheric samples) can be measured. The sensitivity of the turbidimetric analytical procedure is 50 µg of sulfate. Nephelometrically, as little as 2 µg of sulfate can be measured.

REAGENTS

All reagents are made from analytical-grade chemicals.

Hydrochloric acid (10 normal). Dilute 80 ml of concentrated reagent grade hydrochloric acid to 100 ml with distilled water.

Glycerol-alcohol solution. Mix 1 volume of glycerol with 2 volumes of absolute ethyl alcohol (reagent grade).

Barium chloride. Use 20- to 30-mesh crystals.

Standard sulfate solution (100 µg $SO_4^{=}$ per ml). Dissolve 0.148 g of anhydrous sodium sulfate (dry if necessary) in distilled water and dilute to 1 liter.

EQUIPMENT

High-volume sampler. A motor blower filtration system with a sampling head, which can accommodate an 8- by 10-inch glass fiber filter web and is capable of an initial flow rate of about 60 ft^3 per minute, is used and is shown in Figure 6. These samplers are available from General Metals Works, Box 30, Bridgetown Road, Cleves, Ohio; and Staplex Company, 774 Fifth Avenue, Brooklyn 32, N.Y., among others.

Glass fiber filters. Use 8- by 10-inch size, Mine Safety Appliances Company, 1106 BH or any comparable make.[2]

Refluxing apparatus. Use 125-ml flask fitted with reflux condenser and hot plate.

Funnels and Whatman No. 1 filter paper.

Cuvettes. Use cuvettes with a 1-inch light path and plastic stoppers.

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[a] As used by the National Air Sampling Network.

Prepared by Herman A. Iles, Laboratory of Engineering and Physical Sciences, Division of Air Pollution, Public Health Service. Approved by the Interbranch Chemical Advisory Committee, July 1964.

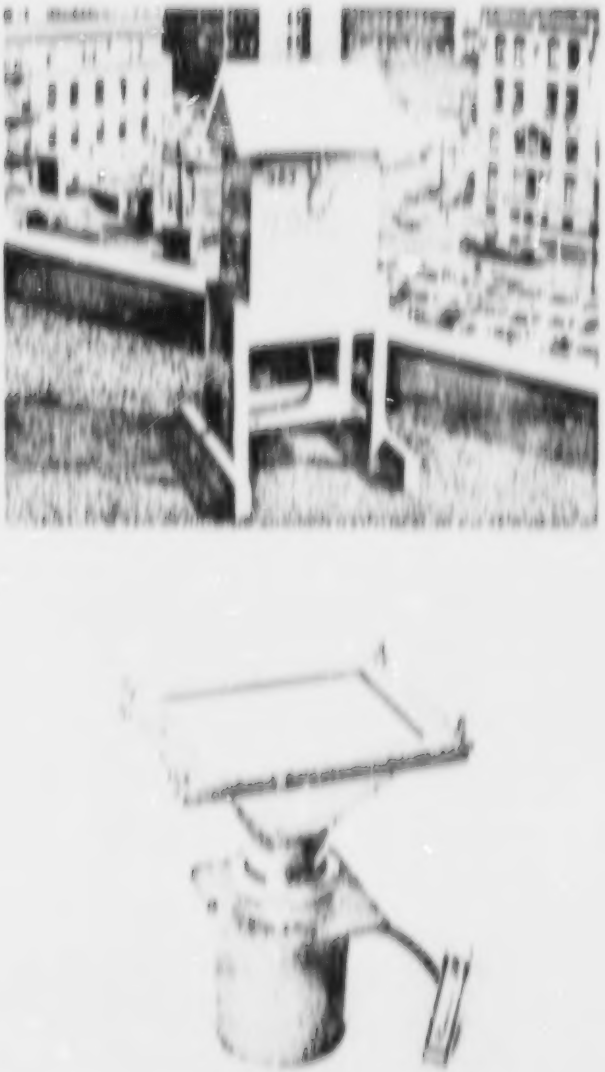

FIGURE 6. TYPICAL SAMPLER ASSEMBLY (ABOVE) AND HIGH-VOLUME AIR SAMPLER (BELOW).

Pipettes. Use 20-, 5-, and 1-ml pipettes.

Spectrophotometer or colorimeter. This device should be suitable for measurement at 500 mμ.

PROCEDURE

Sampling. Using the Hi-Vol sampler, collect the particulates from approximately 2,000 m^3 of air. Twenty-four hours is the usual sampling period. The air volume is calculated from the sampling time and the average of airflow measurements taken at the start and end of the sampling period.

Sample preparation. The sample filter is folded upon itself along the 10-inch axis to facilitate storage and transportation. This folding may result in a nonhomogeneous area in the sample. All sample aliquoting is, therefore, made across the fold. Using a wallpaper cutter or other suitable device and a straight edge, cut a 1-1/4- by 8-inch strip from the filter. Place this in the refluxing apparatus with 45 ml of distilled water and reflux for 30 minutes. Filter through Whatman No. 1 paper, rinsing with distilled water till 50 ml of filtrate is obtained.

Analytical procedure. Place a 20-ml portion of the prepared sample into a clean, dry, 1-inch cuvette. Add 1 ml of 10 N HCl. 4 ml of the glycerol-alcohol solution, and mix. Determine the absorbance at 500 mμ against a reference cuvette containing distilled water. This reading is subtracted from the final reading. It corrects for unmatched cuvettes and other impurities in the sample. Add approximately 0.25 g of barium chloride crystals and shake until dissolved. Let stand for 40 minutes at room temperature (20 to 30°C). Measure the absorbance at 500 mμ against the reference cuvette containing distilled water.

A standard sulfate solution should be analyzed with each batch of samples. Deviations up to 5% from the standard curve can be expected. Occasionally it is advisable to determine the percentage recovery by adding known amounts of sulfate to clean filters and determining the amounts found, using the entire procedure including refluxing. The percentage recovery should be close to 100.

Standardization. Obtain a standard curve by analyzing 20 ml of a series of standards containing 2 to 60 μg $SO_4^=$ per ml. Coordinates of the curve are absorbance and total sulfate in μg (10 to 1,200).

Calculations.

μg $SO_4^=$ per m^3 = FC/V

F = sample aliquot factor = 20

C = number of μg of $SO_4^=$ found

V = sample air volume in m^3

DISCUSSION OF PROCEDURE

Collection media. Although most past data have been reported on Mine Safety Appliance Company glass fiber filters, other filters are available from the Reeve Angel & Company, Union Industrial Equipment Company, Carl Schleicher & Schuell Company, and the Hellman Instrument Company.

Glass fiber filters are not sulfate free. The MSA filters have been found to contain about 4 mg per 8- by 10-inch sheet. It is advisable to check whatever sampling media are used. This sulfate can be removed by water wash prior to sampling if desirable. When this is not practical, results must be corrected accordingly.

The analytical method can also be applied to samples collected on membrane filters and with electrostatic precipitators.

Modification of analytical method sensitivity. To decrease sensitivity, use a smaller sample portion diluted to 40 ml with distilled water. To increase sensitivity, use a larger sample portion or, in extreme cases, measure nephelometrically.

Critical variables and their control. Measurement is dependent upon the amount, the size, and the suspension of the barium sulfate particles.

Parameters that must be controlled are stability of the suspension of colloidal particles, sulfate concentration, barium ion strength, pH, temperature, and aging of the barium chloride solution. Glycerol acts as a stabilizer for the colloid, while alcohol promotes precipitation of the sulfate. Use of solid crystals of $BaCl_2$ eliminates the problem of barium ion strength and solution aging. Sulfate concentration is maintained within the limits of the method, and pH is controlled by addition of HCl. Variations in temperature of 20 to 30°C do not appear to have a significant effect.

Precision of method. The method has been shown to have an 11% coefficient of variation.

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TECHNICON AUTO ANALYZER II

INDUSTRIAL METHOD No. 118-71W/ TENTATIVE — DATE RELEASED: DEC. 1972

SULFATE IN WATER AND WASTEWATER (Range: 0-300 mg/l)

GENERAL DESCRIPTION

In this automated procedure for sulfate, the sample is first passed through a cation-exchange column to remove interferences. The sample containing sulfate is then reacted with barium chloride at a pH of 2.5-3.0 to form barium sulfate. Excess barium reacts with methylthymol blue to form a blue-colored chelate at a pH of 12.5-13.0. The uncomplexed methylthymol blue color is gray, if it is all chelated with barium, the color is blue. Initially, the barium chloride and methylthymol blue are equimolar and equivalent to the highest concentration of sulfate ion expected; thus the amount of uncomplexed methylthymol blue, measured at 460 nm, is equal to the sulfate present.[1]

PERFORMANCE AT 30 SAMPLES PER HOUR

USING AQUEOUS STANDARDS

Sensitivity at 300 mg/l	0.35 absorbance units
Coefficient of Variation at 200 mg/l	0.70%
Detection Limit	10 mg/l

REAGENTS

BARIUM CHLORIDE

Barium Chloride Dihydrate ($BaCl_2 \cdot 2H_2O$)	1.526 g
Distilled Water, q.s.	1000 ml

Preparation:

Dissolve 1.526 g of barium chloride dihydrate in 500 ml of distilled water. Dilute to one liter with distilled water. Store in a brown polyethylene bottle.

METHYLTHYMOL BLUE

Methylthymol Blue[2] 3', 3''-Bis-N, N-bis (carboxymethyl)-Amine Methylthymolsulfonephthalein Pentasodium Salt	0.1182 g
Barium Chloride Solution	25 ml
Hydrochloric Acid, 1.0 *N* (HCl)	4 ml
Distilled Water	71 ml

[1] Lazrus, A.L., Hill, K.C. and Lodge, J.P., "A New Colorimetric Microdetermination of Sulfate Ion"; Automation in Analytical Chemistry, Technicon Symposia, 1965, Mediad, 1966, pp. 301-303.

[2] Eastman Organic Chemicals, Rochester, New York.

Ethanol 3A Reagent Grade, q.s. (C_2H_5OH)	500 ml

Preparation:

Dissolve 0.1182 g of methylthymol blue in 25 ml of barium chloride solution. Add 4 ml of 1.0*N* hydrochloric acid, which changes the color to bright orange. Add 71 ml of water, and dilute to 500 ml with ethanol. The pH of this solution is 2.6. Store in a brown glass bottle. Prepare this reagent fresh daily.

BUFFER, pH 10.5 ± 0.5

Ammonium Chloride (NH_4Cl)	6.75 g
Ammonium Hydroxide, conc. (NH_4OH)	57 ml
Distilled Water, q.s.	1000 ml

Preparation:

Dissolve 6.75 g of ammonium chloride in 500 ml of distilled water. Add 57 ml of concentrated ammonium hydroxide and dilute to one liter with distilled water. Store in a brown polyethylene bottle.

BUFFERED EDTA

Tetrasodium EDTA	40 g
Buffer, pH 10.5, q.s.	1000 ml

Preparation:

Dissolve 40 g of tetrasodium EDTA in pH 10.5 buffer and dilute to one liter with buffer. Store in a brown polyethylene bottle.

SODIUM HYDROXIDE, 0.18 *N*

Sodium Hydroxide (NaOH)	7.2 g
Distilled Water, q.s.	1000 ml

Preparation:

Dissolve 7.2 g of sodium hydroxide in 800 ml of distilled water. Allow to cool and dilute to volume with distilled water.

STANDARDS

STOCK SULFATE STANDARD, 1000 mg/l

Sodium Sulfate, anhydrous (Na_2SO_4)	1.479 g
Distilled Water, q.s.	1000 ml

Preparation:

Dissolve 1.479 g of sodium sulfate in 500 ml distilled water. Dilute to one liter with distilled water.

Printed in U.S.A. by Technicon Instruments Corporation, Tarrytown, New York

WORKING STANDARDS

ml Stock	mg/l $SO_4^{=}$
1.0	10
6.0	60
12.0	120
18.0	180
24.0	240
30.0	300

Preparation:

Pipette stock into a 100 ml volumetric flask. Dilute to 100 ml with distilled water.

ION EXCHANGE COLUMN

The column consists of a length of glass tubing 7.5 inches long, 2.0 mm ID and 3.6 mm OD. The commercial ion-exchange resin Bio-Rex 70,** 20-50 mesh, sodium form is freed from fines by stirring with several portions of deionized water and decanting the supernate before settling is complete. Fill the column with resin, taking care that air is not trapped in the column. Glass wool plugs are placed at each end to prevent the resin from escaping. Care should be exercised that excess glass wool is not used which will cause back pressure.

OPERATING NOTES

1. When running this system, it is very important that no air bubbles enter the ion-exchange column at any time. If air bubbles become trapped, it is advisable that the column be prepared over again.

2. Cations, such as calcium, aluminum, and iron, interfere by complexing the methylthymol blue. These ions are removed by passage through an ion-exchange column.

3. Before running this method, position the controls of the Modular Printer as follows:

CONTROL	POSITION
MODE Switch	Normal
SAMPLING RATE Switch	30
RANGE Switch	300
DECIMAL Switch	000.

Details of Modular Printer Operation are provided in Technical Publication No. TA1-0278-10.

4. Since this chemistry does not conform to Beer's Law, a Technicon Linearizer is necessary in order to obtain readings which are directly proportional to concentration.

When using the Linearizer, a non-linearized calibration curve is first plotted by placing the Linearizer in the direct mode. Using the non-linear curve, concentrations of standards are selected which fall at approximately 75% for each range of the Linearizer. For example, a concentration which falls at 15% of scale in the non-linearized mode should be selected as the standard for the 0-20% range of the Linearizer. These concentrations as calculated are then used to set the Linearizer as directed in the Linearizer manual (Technicon No. TA1-0279-00).

5. At the end of each day, the system should be washed with a solution of EDTA. This may be done by placing the methylthymol blue line and the sodium hydroxide line in water for a few minutes and then into the tetrasodium EDTA for 10 minutes. Wash system with water for 15 minutes before shutting down.

6. Alternate ranges may be obtained by utilization of the Std Cal control on the Colorimeter.

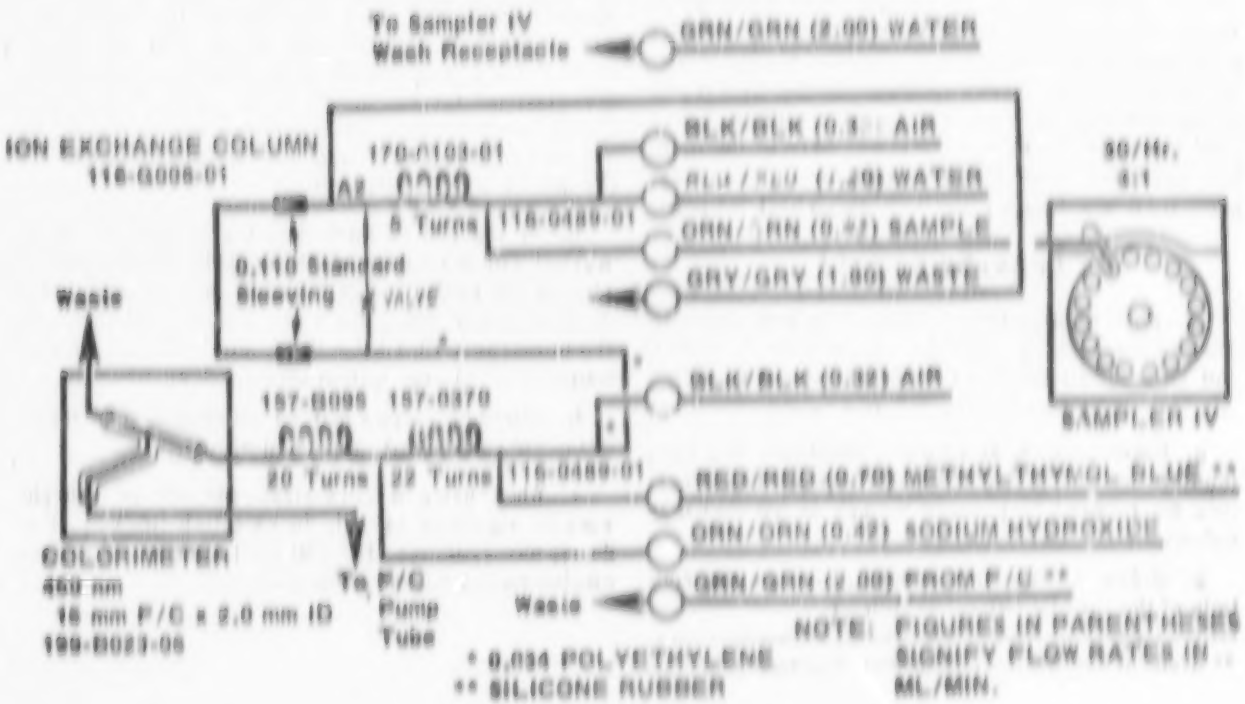
7. When using a Linearizer, the use of multiple working standards is only to establish linearity. For day-to-day operation, the 180 mg/l standard is recommended for instrument calibration.

** Available from Bio-Rad Laboratories, Richmond California.

SULFATE IN WATER AND WASTEWATER

(Range: 0 - 60 mg/L)

MANIFOLD NO. 116-0096-01



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A DIVISION OF TECHNICON INSTRUMENTS CORPORATION

APPENDIX C

A MICROMETHOD FOR SULFATE IN ATMOSPHERIC PARTICULATE MATTER

AIHL REPORT NO. 163

Prepared by:

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2151 Berkeley Way
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July 1974

INTRODUCTION

The increased concern with the biological effects of particulate sulfate and the need to determine diurnal patterns spurred the study for a fast and sensitive micromethod for analysis of sulfate in atmospheric particulate matter.

Despite new instrumental methods, some cations and anions must still be analysed by wet chemistry. Hi-vol filter mats generally have a substantial amount of material collected which allows the use of macro techniques (mg amounts) for the determination of the analytes. However, if samples have been collected at low air flow rates and for short periods, the techniques to be applied must be refined and selected accordingly.

In this paper we present a review of existing procedures for sulfate analysis, a number of which were considered and rejected as inadequate for further development. Following, a micromethod is detailed which extends the working range for $SO_4^=$ down to nearly 1 ug/ml of extract.

SUMMARY OF SULFATE METHODOLOGY

Sampling and extraction are very important steps in the determination of sulfate. When determining sulfate from particulate matter collected on glass fiber filters, low values are to be expected because of

retention of sulfate on glass (1). Analytical losses vary inversely with the sulfate concentration per unit area. The retention of sulfate when using glass fiber filters is believed to be caused by the barium content of the glass. Therefore, organic filters are to be preferred for low amounts of sulfate (< 50 ug). The collection efficiency of membrane filters is very high even at relatively large nominal pore sizes (2). A good recovery of sulfate from the filters has been obtained by using a microextraction procedure which utilizes 5 ml of distilled water in a small flask (3,4).

Analyzing low concentrations of sulfate has been accomplished in the past by concentrating large samples and determining precipitated barium sulfate gravimetrically (5,6,7). Gravimetry is still used where high accuracy is of prime concern. A step toward simplifying these procedures and expanding the capabilities on smaller samples has been made by using turbidimetry or nephelometry of barium sulfate (6,8,9,10) or organic sulfates such as benzidine (11), amino-chlorobiphenyl (12,13), and aminoperimidine (11,13,14,15).

Titration methods were proposed for increasing the accuracy over turbidimetric methods. The most popular method, refined to be usable in the range of 2 to 10 ug/ml, titrates the sulfate in 80% ethanol with 0.005 M Ba^{++} using Thorin as indicator (16). Because of the difficulty in observing the endpoint, the use of photometric titration has been suggested (17). Sharper endpoints are obtained using Sulfonazo III (18) and Nitrochromazo (19) as indicator. In a study made comparing different

indicators it has been shown that the indicator Dimethylsulfonazo III is best suited for titrimetry with barium for visual endpoint estimation (20). Dimethylsulfonazo III has been collaboratively tested as an indicator in Ba titration of sulfate after separation of cations with a cation exchange resin (21). It has been observed that pH plays an important role in the formation of initial crystallization centers which speed up the equilibrium of the reaction during titration. The best buffer was a combination of pyridine with a strong acid (22) in an almost anhydrous organic solvent. Pyridine seemed to produce solvolysis of the indicators. A similar solvolysis effect has been observed with surfactants (23).

A lead-sensitive electrode has also been used for determining the endpoint in the titration of sulfate in dioxane using a dilute lead solution (24,25). Exchange resins can be used to eliminate interferences for this technique (26). Some methods are based on the exchange of the anion bound to Ba with sulfate. The popular chloranilate method (27,28) has been modified to eliminate interferences caused by some cations and to stabilize the variable sensitivity to changes of pH (29). It has been adapted for use in automated systems (30).

Other exchange methods use barium iodate. After exchange with sulfate the solubilized iodate is used to oxidize iodide to iodine. Either the triodide ion is measured directly (31) or reacted with cadmium iodide – linear starch (32). Interference from calcium in these methods is sometimes a problem, because only 15% of the calcium sulfate reacts (31).

Two general sulfate reduction methods to H_2S are available. One reduces sulfate with HI and hypophosphorous acid (33,34,35) and the other uses stannous phosphate in excess phosphoric acid (36,37). The hydrogen sulfide so generated can be quantitated with very sensitive reagents which offer a high degree of specificity. The most sensitive techniques for analyzing H_2S are fluorescence quenching (38,39,40), silver-dye exchange (41,42), methylene blue formation (34,37,43), and molybdenum reduction (44).

Indirect titration methods, reacting an excess Ba^{++} with the sulfate and determining the unreacted barium by atomic absorption (45) or by a colorimetric procedure using methyl thymol blue has been proposed. The latter method was automated and employed extensively for sulfate analysis of samples collected by the National Air Sampling Network. Flame photometry (46) and thermogravimetry, which are still in the developmental stage, are sensitive direct procedures for sulfate.

SUMMARY OF THE AIHL MICROCHEMICAL SULFATE METHOD

In selecting an appropriate method the aim was to achieve a compromise between simplicity, specificity and accuracy. The limitation imposed for the selection of a method in the present study was the amount of sulfate encountered in aqueous extracts of membrane filters obtained from sampling 10 m^3 of air. Therefore, the method must be capable of furnishing acceptable information in the low microgram range. Samples

were collected on preweighed cellulose ester membrane filters. Extractions were performed by a micropercolation technique using a minimal amount of liquid. The principle of the barium-dye exchange method was selected for measurement. The substance used as barium salt for the reaction was the complex formed with nitrochromeazo [2,7 - bis (4-nitro-2-sulfo-phenylazo) - 1,8 dihydroxynaphthalene - 3,6 disulfonic acid sodium salt] (19,49). A procedure based on the same principle has been described recently (50). The reaction employed may be symbolized as follows:

$$Ba\text{-dye} + SO_4^{=} \rightarrow BaSO_4 + Dye$$

The barium-dye complex exhibits an absorbance maximum at 640 to 645 nm in pH 5,6 buffered acetonitrile while the unassociated dye absorbs less at this wavelength. By using an excess of the barium-dye complex relative to the expected sulfate level, the decrease in absorbance at 640 to 645 nm can be directly measured against a reagent blank in a double beam spectrophotometer and related to the sulfate concentration.

EXPERIMENTAL

A. Apparatus

-- A double beam spectrophotometer with 2 nm bandpass and 10 mm pyrex glass cuvettes are suitable.

-- Variable volume micropipets (0-20 µl, 0-200 µl, 0-1,000 µl).

-- Glass stoppered test tubes 16 X 150 mm.

B. Chemicals

-- Nanograde acetonitrile free of traces of sulfate and metals. Each batch of this solvent must be tested for sulfate before use.

-- Barium chloride. The chloride is preferable to the perchlorate which is hygroscopic.

-- Nitrochromeazo (also called Nitrosulfonazo III). This product is available from different sources[4]. In the formulation of the reagent a 50% molar excess over Ba is used in order to compensate for the less than 100% dye content.

-- Pyridine, AR.

-- Benzene sulfonic acid, monohydrate. The Eastman Kodak No. 2313, low in heavy metals, is satisfactory.

-- Sodium sulfate anhydrous. Dry in an oven for one hour at 105°C in a weighing bottle. Close bottle with glass stopper while hot and leave to cool in a dessicator.

C. Reagents

-- 0.01 M $BaCl_2$ aqueous.

-- 0.001 M $BaCl_2$ aqueous.

-- 0.15% Nitrochromeazo, aqueous (approximately 0.0015 M).

-- Buffer pH 5.4. Dissolve benzenesulfonic acid monohydrate in water to obtain a 50% w/v solution. To 25 ml of 50%

[4] Pfaltz and Bauer, Gallard-Schlesinger, K + K, Fluka, Aldrich.

benzenesulfonic acid add 12 ml pyridine, then cool and make up to 100 ml.

-- Reagent mixture. In a 1,000 ml volumetric flask place 850 ml acetonitrile and add:

20 ml 0.001 M $BaCl_2$ solution

25 ml 0.15% Nitrochromazo solution

10 ml buffer pH 5.4

Fill to mark with water. The apparent pH of this solution is 5.4.

-- Sulfate stock solution, 1,000 µg/ml sodium sulfate: Dissolve 1.479 g dried Na_2SO_4 in one liter of distilled water.

-- Sulfate standard solution, 20 µg $SO_4^=$ per ml. Dilute 2.00 ml sulfate stock solution to 100 ml.

D. Procedure

1. Sample preparation and approximate estimation of sulfate content.

The air is preferably sampled with preweighed cellulose ester membrane filters. After weighing, the approximate amount of sulfate collected is estimated from XRF data if available or from statistical information on sulfate as a percent of total mass obtained from previous studies in the same or adjacent areas under similar sampling conditions. Generally, the range for sulfate found on the west coast is between 2 and 20 $\mu g/m^3$

with most values at the lower quartile, or between 3 and 10% of the total amount of particulate material collected.

2. Extraction.

Cut each filter with a scalpel holding it with tweezers and insert the pieces into a fritted disc funnel. A flask containing 5 ml of distilled water and stoppered with a one-hole rubber stopper holds the fritted disc funnel whose stem reaches the bottom of the flask (3). Heat repeatedly with an aluminum block or a microburner. To insure complete extraction 3 micropercolations were used. The extract may be used for determination of sulfate, nitrate and eventually other water-soluble products. Alternatively, heat screw cap test tubes containing 5 ml of water and filter to 80°C for two hours in an oil bath. After shaking occasionally allow the tubes to cool overnight. This technique gave 10% less recovery than the micropercolation extraction technique.

3. Sulfate determination.

Pipet aliquots of one ml or less of the aqueous extracts blanks and standards containing approximately 6 to 10 ug $SO_4^{=}$ into a glass-stoppered test tube (16 X 150 mm). Dilute the aliquots to 1 ml with water with the 1.00 ml variable volume micropipet. Then add 8 ml of the reagent mixture, shake and allow one hour reaction time in a cool, dark place. Read the absorbance in a 10 mm cell at the

peak between 640 and 645 nm in the double beam spectrophotometer against a blank prepared with 1 ml distilled water.

4. Calibration.

Place aliquots from the dilute standard solution into glass stoppered test tubes (16 X 150 mm) so as to cover a measuring range between 1 and 14 µg, and bring each to one ml with distilled water. Alternatively, add small aliquots of the concentrated stock solution to one ml of distilled water with the aid of micropipets. Then add 8 ml of the reagent mixture and proceed as indicated above. Construct a calibration graph with absorbance on the ordinate and µg sulfate on the abscissa. The origin of the line should go through zero. A least square line is calculated.

5. Measurement.

The calibration curve was a straight line from the origin up to absorbance 0.6, which corresponded to approximately 12 µg $SO_4^=$. Above 14 µg/ml $SO_4^=$ the curve begins to flatten, and below 6 µg $SO_4^=$ there seems to be a larger error on real samples although the standard curve is linear to one µg or below.

6. Effect of interferents.

Calcium is a serious interference, since the exchange of Ba by Ca in the complex does not affect the color of the

complex significantly. For 10 ug of sulfate and a molar ratio of 0.1 Ca/SO_4 the loss in response was 45%; at a molar ratio of 1 Ca/SO_4 the loss was 90 to 95%, whereas at a molar ratio of 20 Ca/SO_4 the loss in response was total. Atmospheric samples collected in Los Angeles, however, contained only a small amount of soluble Ca which resulted in losses of 4 to 10%.

7. Intermethod comparison.

Hi-vol aqueous extracts of atmospheric particulate matter saved from previous turbidimetric analyses were used for intermethod comparisons. These extracts were combined so as to obtain four different concentrations in the range of 10 to 40 ug/ml and analyzed by two methods, i.e., turbidimetric $BaSO_4$ and titrimetric with a photometric endpoint using the same dye as for the colorimetric procedure. The titration was made in quadruplicate with 0.001 M $BaCl_2$. The turbidimetry of $BaSO_4$ and this method were made in triplicate. Results are shown on Table 1.

It can be observed that the mean relative standard deviation is largest for the micromethod and smallest for the titrimetric procedure. Both the micromethod and the turbidimetric procedure have larger deviations at the lower concentrations, whereas the titrimetric procedure has higher precision at lower concentrations. Higher values are obtained for the

titrimetric procedure at the lower levels, which is explainable by the relatively higher solubility of $BaSO_4$ at low concentrations which affects more of those methods based on a strict solubility equilibrium.

The micromethod has a consistently lower value (~ 4 µg/ml) at all concentrations possibly due to solubility of $BaSO_4$ which seems to be greater for atmospheric sample extracts than for the solutions prepared from pure aqueous standards.

DISCUSSION

A. Other Methods

Aminoperimidine was interfered by coextracted organic substances which promoted premature agglomeration and precipitation of the suspension. This fact was not observed with pure solutions. Exchange methods which relied on the measurement of iodine were not considered because of possible interference by reductants and chromophores in atmospheric extracts.

Measurement of hydrogen sulfide obtained by reduction of sulfate was considered cumbersome and inappropriate.

B. AIHL Methods

1. Limitations

Since this is a differential method, the precision is critically dependent upon adjusting sample aliquot size to an optimum range.

As conducted in the present study, the solution containing the barium-dye complex had the capacity of reacting with a maximum of 15 $\mu g/SO_4^{=}$. The optimum aliquot size for this capacity contained between 6 and 10 μg $SO_4^{=}$. This requirement represents the most serious limitation of the method.

Sulfate introduced spuriously shortens the range of the method and affects precision. Glassware used for all tests should be scrupulously clean. Reagents must be tested for sulfate content. New batches of solvents (acetonitrile, pyridine) and reagents must be compared to the old set of reagents in order to establish performance. Solvents containing more than 100 μg SO_4/liter or reagents which introduce more than one $\mu g/SO_4$ per determination should be replaced.

The negative effect due to calcium could be reduced by addition of 0.05 ml of a 20% citric acid solution. This observation was made during titrimetry of $CaSO_4$ but no experimental data was obtained for the micromethod. Another approach used previously is the removal of interfering cations by ion exchange.

2. Variations

From the various organic solvents proposed for the exchange reaction, acetonitrile offered the lowest solubility product for $BaSO_4$ and fastest stabilization, thus gave more reliable

information at the lowest levels of sulfate. Eighty percent acetone could not be used because of large variations apparently caused by a slower reaction rate.

It has been shown that at a pH of 5 to 6 all dyes react fastest in organic-water medium. In principle, this value of pH can be obtained in many different ways, e.g., with pyridine and acetic acid (18). However, we have observed that equilibration between available $SO_4^{=}$ and Ba^{++} in an aqueous-organic mixture works fastest when the anion ionizes readily. This approach has been used unwittingly when using a buffer composed of pyridine and perchloric acid (22). The hazardous nature of perchloric and nitric acids are known when they come in contact with organic solvents. Therefore, benzene sulfonic acid was selected as a substitute although toluene sulfonic acid and trichloroacetic acid worked as well.

Small changes in the water content of the final solution between 15 and 30% affected the response at the level from 0 to 1 µg/ml, which is apparently caused by increased solubility of the $BaSO_4$ produced. If the water content of the reagent or the final mixture falls below 15%, precipitation of the Ba-dye complex may occur.

3. Measurement and standards

The use of variable micropipets was very convenient for working with aliquots under one ml. The accuracy of the pipets we used was found to be better than 1%.

Better accuracy for the method is obtained in the upper range. Below 6 µg $SO_4^=$ an asymptotic increase in % relative error has been measured. This effect is a result of $BaSO_4$ solubility and reaction speed. The slope of the calibration curve depends on the relative amount of sample, reagent and time but is essentially a straight line when fixing these paramet: The water content of the final mixture and the absolute content of Ba^{++} and complexant also affects the slope. When the molar concentration of Ba in the reagent is approached or exceeded by the $SO_4^=$ content, the calibration curve is no longer linear and flattens out. Therefore, accuracy is highest on a narrow range of 6-14 µg per determination.

Before final readings were made, a technique was tried which consisted of reducing the final apparent value of pH from 5.4 to below 3.5 in order to reduce blank values. When comparing the reacted mixture with the reagent blank on a double beam spectrophotometer, no significant differences were observed on real samples whether measuring the absorbance at one or another pH value. In cases where the optical mechanism of an instrument is not capable of measuring differences at high values of

absorbance (differences of tenths in a background of about absorbance 3) the shift to a lower pH before readings may be necessary.

4. Intermethod Comparisons

Several dyes of similar composition have been evaluated for the titrimetry of sulfate in the microgram range (20). Although not adequate for the visual titration step, nitrochromeazo was selected because of its highest molar absorptivity (1V) and fastest equilibration when reacting with Ba. The titration was carried out using pyridine-benzenesulfonic acid buffer and 66% acetone. The color change at the equivalence point was compared to two identical Erlenmeyer flasks containing all the reagents but Ba in one and 0.5 ml excess of 0.001 M Ba in the other. The reason for using 66% acetone in preference to 80% propanol is because it is less affected by variations of solvent concentration, and less toxic.

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TABLE 1. COMPARISON OF MICRO AND MACRO SULFATE ANALYSES WITH ATMOSPHERIC PARTICULATE SAMPLES

	Micro-$SO_4^{=}$[a]		Titrimetric $SO_4^{=}$[b]		Turbidimetric $SO_4^{=}$[c,d]	
Sample	μg/Aliquot	μg/ml	μg/Aliquot	μg/ml	μg/Aliquot	μg/ml
S_1	1.7±0.2	7.3±0.4	570±6	11.4±0.1	510±5	10.5±0.3
S_2	3.5±0.3	7.8±0.6	580±12	11.6±0.2	505±7	10.1±0.4
S_3	4.6±0.3	11.4±0.7	855±20	17.1±0.4	695±20	14.8±1.0
S_4	8.1±0.1	20.3±0.4	1145±35	22.9±0.7	484±8	24.2±0.4
S_5	6.8±0.2	30.8±1.1	2535±52	32.7±1.0	723±5	36.1±0.3

[a]Data shown represent mean values and 1σ values for 3 replications of each sample.
[b]Data obtained from 4 replications of each sample.
[c]Reference (5).

Appendix D

PROTOCOL FOR THE MODIFIED BROSSET PROCEDURE FOR SULFATE DETERMINATION

A. Introduction

The original method[1,2] was assembled and modified. This procedure was employed with atmospheric samples collected on filter media. Sulfate was removed by aqueous extraction techniques discussed in Sections V and VI. In the present study, dilution of the extracts was necessary to provide samples within the working range of this method, ca. 2-10 ug/ml sulfate. The degree of dilution necessary was established by preliminary analysis with a second sulfate method.

The procedure contains two parts: ion exchange treatment for removal of cationic interferents and reagent addition plus spectrophotometric determination.

B. Chemicals and Equipment

1. Chemicals

Amberlite SA-2 ion exchange paper (Reeves Angel, strong acid form)

Adipic Acid (Fisher certified)

Acetone (Fisher ACS certified)

Thorin (Baker's analyzed reagent)

Barium perchlorate, anhydrous (Pfaltz and Bauer)

$CoSO_4 \cdot 7H_2O$

$NiCl_2 \cdot 6H_2O$

$CuSO_4 \cdot 5H_2O$

72% Perchloric acid (Baker's analyzed reagent)

2. Diluent Solution

Dissolve 10 g adipic acid in about 500 ml acetone. Add 10 ml of a solution containing 525 mg anhydrous $Ba(ClO_4)_2$ in 250 ml 0.1 N $HClO_4$ to the adipic acid in acetone and make up to a volume of 1 liter with acetone.

3. Reagent Solution

Dissolve 250 mg Thorin in 10 ml 0.01 N H_2SO_4 and bring up to 100 ml with distilled water. In a red glass bottle, this solution showed no signs of deterioration after 6 weeks.

4. Grey filter solution

100 ml of grey filter solution was prepared with 1.5 g $CoSO_4 \cdot 7H_2O$, 1.0 g $CuSO_4 \cdot 5H_2O$ and 4.0 g $NiCl_2 \cdot 6H_2O$.

5. Ion exchange filter discs

Circular filter discs were punched out of the ion-exchange paper sheets by means of a 5/8" "Arch" Punch. The filter discs were soaked overnight in one liter of 4% HCl, then washed four times with two liters of glass distilled water over an eight hour period. The discs were spread out individually on a sheet of Saran wrap and allowed to air dry overnight in a laminar flow clean bench. Tweezers were used to insert three discs in each of a series of plastic syringe bodies.

6. Equipment

Plastic syringe bodies ("Monoject" 12 cc, Catalogue No. 5128)

25 ml beakers

"Rainin" adjustable pipet (0-5 ml)

"Rainin" adjustable pipet (0-200 ul)

Repeatable 5 ml dispensing pipet (Repipet)

C. Ion Exchange Treatment[A]

Add about 3 ml of the sample solution to the filter discs contained in

[A] (Therma J: Combined ion-exchange - solvent extractio of metal ions on ion-exchange papers, Separation Science 2 177 (1967)

the syringe bodies and allow to slowly drip through the discs into a 25 ml beaker. Replace the syringe plunger and depress to remove an additional amount of the solution if necessary. Separate sets of ion exchange filter discs are used for each sample.

D. Reagent Addition and Spectrophotometric Determination

Transfer 3 ml of the treated sample solution, using the 0-5 ml Rainin pipet to a 2.5 cm cylindrical quartz cell. Add 0.125 ml of reagent solution using a 0-200 µl Rainin petpet followed by 5 ml of diluent dispensed from the automatic pipet (Repipet). After capping the cell, start a timer and shake 5 to 10 times. Read the contents of the cell after one minute at 520 nm. The zero is set to absorbance 0.800 by replacing the sample solution with distilled water. A double beam spectrophotometer was used with a stable grey filter solution in the reference beam light path. The quartz cell is drained, but not rinsed, between samples.

The calibration was made by using 3 ml of standard solutions containing from 0 to 10 µg/ml sulfate, prepared by stepwise dilution of a more concentrated (1000 µg $SO_4^=$ per ml) solution. This solution was made with oven-dried sodium sulfate.